Supporting information

Unlocking the Accessibility of Alkyl Radicals from Boronic Acids through Solvent Assisted Organophotoredox Activation

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1.1. General information

All components as well as reagents and solvents were used as received without further purification, unless stated otherwise. Reagents and solvents were bought from Sigma Aldrich and TCI and if applicable, kept under argon atmosphere. Technical solvents were bought from VWR International and Biosolve, and are used as received. Product isolation was performed using silica (60, F254, Merck™), and TLC analysis was performed using Silica on aluminum foils TLC plates (F254, Supelco Sigma-Aldrich™) with visualization under ultraviolet light (254 nm and 365 nm) or appropriate TLC staining. ^{1}H (400MHz or 500 MHz), ^{13}C (100MHz) and ^{19}F (376 MHz) NMR spectra were recorded at ambient temperature using a Bruker-Avance 400 or Mercury 400. ^{1}H NMR spectra are reported in parts per million (ppm) downfield relative to $CDCl_3$ (7.26 ppm), ^{19}F NMR spectra are reported without internal standard with C-F/C-H decoupling and all ^{13}C NMR spectra are reported in ppm relative to $CDCl_3$ (77.2 ppm). NMR spectra uses the following abbreviations to describe the multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, hept = heptet, m = multiplet, dd = double doublet, td = triple doublet. Known products were characterized by comparing to the corresponding ^{1}H NMR and ^{13}C NMR from literature. GC/MS analyses were performed using the gas chromatographer (Thermo Finnigan Trace GC Ultra 2.2) equipped with a GC capillary column (Restek Rxi-5ms 30m, 0.25mm ID, 0.25µm df) and coupled to a mass spectrometer (Thermo Fisher ITQ 900 2.2, with electron ionization (EI) and ion trap mass analyzer) using an auto sampler unit (Thermo Quest AS 2000). The system was set at an oven temperature of 300 °C and a ramp rate of 20 °C/min; split/splitless inlet (SSL) injector temperature of 250 °C, split flow 60 ml/min and split ratio 50; MS transfer line at 300 °C. High resolution mass spectra were acquire on a quadrupole orthogonal acceleration time-of-flight mass spectrometer (Synapt G2 HDMS, Waters, Milford, MA). Samples were infused at µl/min and spectra were obtained in positive ionization mode with a resolution of 15000 (FWHM) using leucine enkephalin as lock mass. Melting points were determined with a Buchi B-540 capillary melting point apparatus in open capillaries and are uncorrected.

Chemicals: DMF (99.8%, extra dry), DMA (99.8%, extra dry) and DMSO (99.8%, extra dry) were purchased from Acros Organics and used as purchased. HMPA, NMP, DMPU and Et_3N were also used as purchased. The transition metal photocatalysts $Ru(bpy)_3(PF_6)_2$ and $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ were purchased from commercial sources. The organic photocatalyst

4CzIPN was prepared in lab by the procedure outlined in previous publications.[1] Perfluoroalkylsubstituted alkenes were prepared in lab by reported procedures outlined here. Deuterated solvents were used as purchased (DMSO-d_6, DMF-d_7).

Photochemical experiments were performed magnetically stirred in 10 mL glass test-tubes with screw cap equipped with silicon septa. The tubes were irradiated with blue light (450 nm) using a coiled commercial LED strip fixed in 3D-printed reactor (1 m, from LEDXON, PN: 9009083) with a total power output of 14.0 W. To maintain a constant reaction temperature of 30°C, the setup was cooled by a constant air flow (Figure S1, A, B). Flow experiments were performed using a Vapourtec E-Series photoreactor (UV-150) (Figure S1, C).

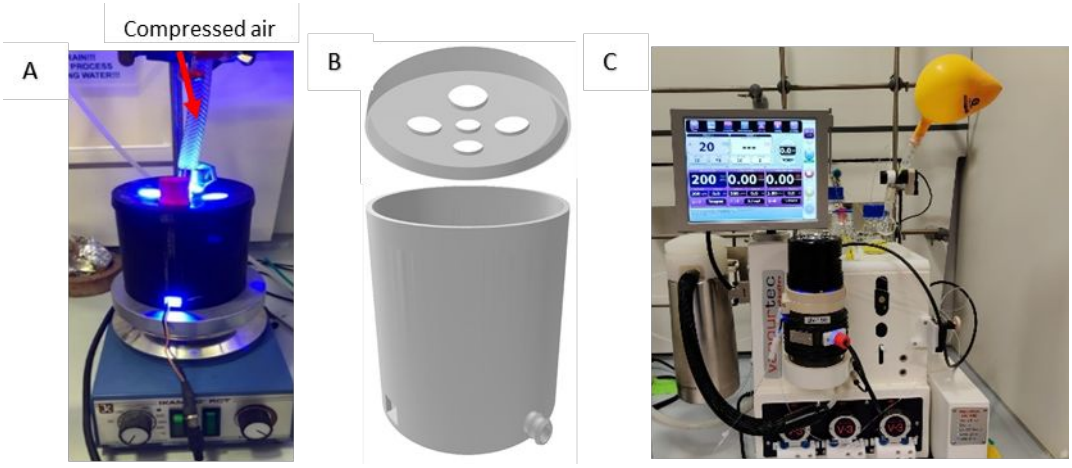
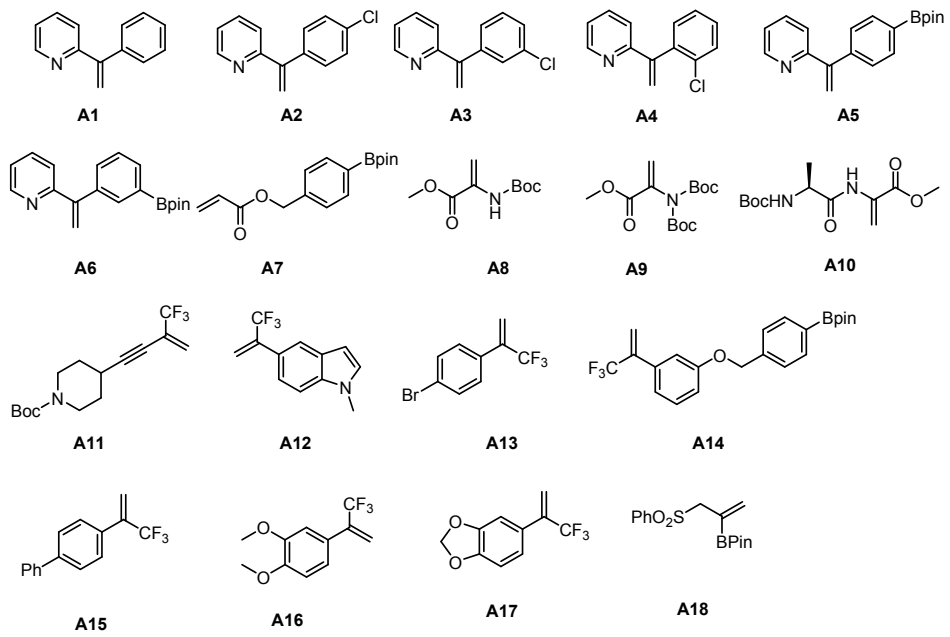


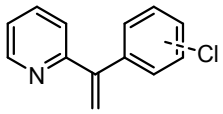
Figure S1: Reaction setup (in-house 3D printed reactor and flow reactor).

1.2. Synthesis and characterization of starting materials

Alkene acceptors **A1**[2], **A2-A4**[3], **A5-A6**[4], **A7**[5], **A8**[6], **A9**[7], **A10**[8], **A11**[9], **A12-15**[10], **A16-17**[11] and **A 18**[12] were synthesized according to previous literature. **A5-A6** were synthesized by modified procedure.



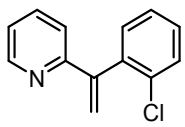
Compound A2-A4



In a flame dried 20 mL screw cap vial with silicon septa, *N*-tosylhydrazone (1.5 mmol, 1.5 equiv), $PdCl_2(MeCN)_2$ (0.05 mmol, 5 mol%) and 1,1′-bis(diphenylphosphino)ferrocene (DPPF) (0.1 mmol, 10 mol%) were added. The reaction vial was degassed and purged with Ar (repeated 2 times). Dry 1,4-dioxane (3 mL) was added into the reaction mixture and stirred for 30 min.. Afterwards, LiO^tBu (2.2 mmol, 1.5 equiv) was added into the reaction vial and Ar was purged again into the vial before adding 2-bromopyridine (1.0 mmol). The resulting reaction mixture was placed in a preheated oil bath at 100 °C in a sealed tube for 3 h. After completion, the reaction mixture was diluted with EtOAc and filtered through celite. The solvent was evaporated under reduced pressure and the crude residue was purified by flash chromatography on silica gel.

TLC : 10% EtOAc in heptane
Column: gradient from 3% - 10% EtOAc in heptane

Compound A4

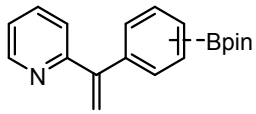


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.62 (m, 1H), 7.60 (td, J = 7.8, 1.8 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.34 (m, 2H), 7.18 (ddd, J = 7.5, 4.8, 1.0 Hz, 1H), 7.08 (d, J = 7.9 Hz, 1H), 6.45 (d, J = 1.5 Hz, 1H), 5.51 (d, J = 1.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.73, 149.46, 147.12, 139.76, 136.50, 133.45, 131.71, 129.72, 129.19, 127.01, 122.44, 121.50, 119.92,

HRMS (ESI^+): $[M+H]^+$cal'd for $C_{13}H_{11}ClN$:216.05744 found: 216.0584

Compound A5-A6

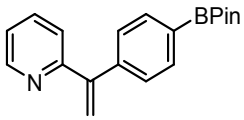


In a flame dried 10 mL reaction vial, (hetero)aryl chloride (0.4 mmol, 1.0 equiv), Xphos (2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl) (10 mol%), $Pd(OAc)_2$ (4.48 mg, 0.02 mmol, 5 mol%), bis(pinacolato)diboron (121 mg, 0.48 mmol, 1.2 equiv), and anhydrous KOAc (78 mg, 0.8 mmol, 2.0 equiv) were added. The reaction vial was then purged with nitrogen followed by dry dioxane (1.3 mL). The resulting reaction mixture was then placed in a preheated oil bath at 80 °C and stirred for 12 h. Afterwards, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (10 mL) and washed with brine. The resulting aqueous phase was extracted with ethyl acetate (20 mL × 3). The resultant organic phases were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The solvent was evaporated under reduced pressure and the crude residue was purified by flash chromatography on silica gel.

TLC : 20% EtOAc in heptane (Rf = 0.4)

Column: gradient from 3% - 15% EtOAc in heptane

Compound A5



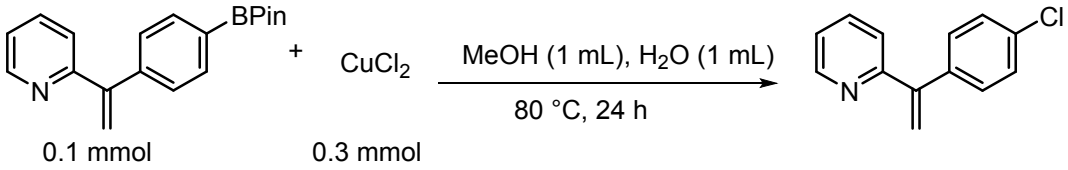
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (ddd, J = 4.8, 1.8, 1.0 Hz, 1H), 7.82 – 7.78 (m, 2H), 7.59 (td, J = 7.8, 1.8 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.22 – 7.16 (m, 2H), 6.02 (d, J = 1.4 Hz, 1H), 5.61 (d, J = 1.4 Hz, 1H), 1.33 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.21, 149.36, 148.91, 143.20, 136.44, 134.84, 127.78, 122.98, 122.58, 118.43, 83.85, 24.87.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.37.

HRMS: We could not observe the exact mass in HRMS in ESI (positive and negative mode) and APCI positive mode.

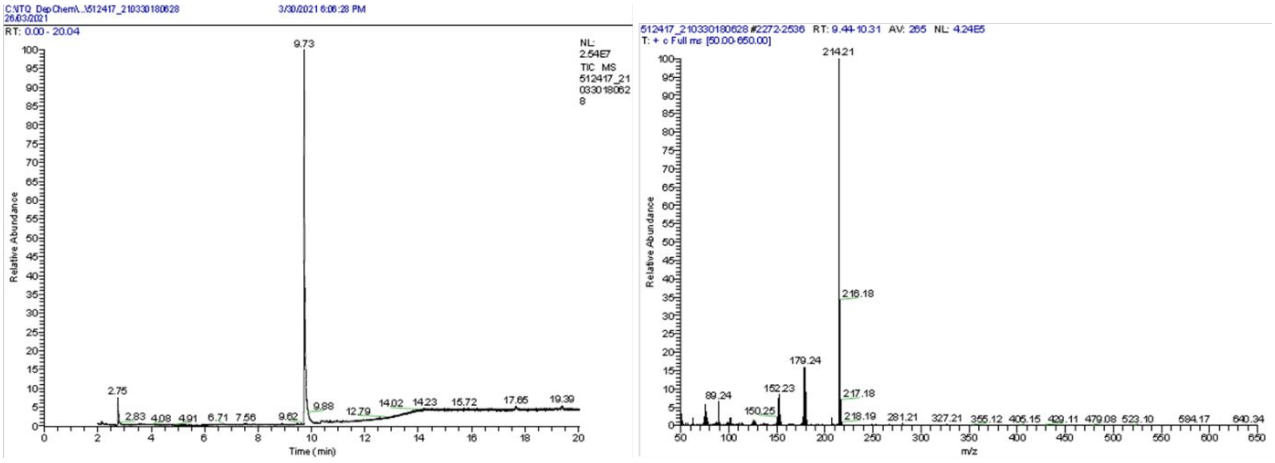
To further confirm the structure, we performed halodeboronation following the reported procedure:[13]



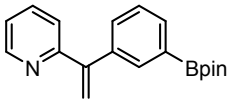
In a flame dried 10 mL reaction vial, compound **A5**, $CuCl_2$, MeOH and H_2O were added. The resulting reaction mixture was then placed in a preheated oil bath at 80 °C and stirred for 24 h. Afterwards, the reaction mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and washed with H_2O, aqueous HCl (1.0 M, 10 mL) and brine (10 mL). The organic phases was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The solvent was evaporated under reduced pressure and the crude residue was purified by flash chromatography on silica gel.

Column: gradient from 3% - 10% EtOAc in heptane

Spectroscopic data were consistent with literature values.[2]



Compound A6



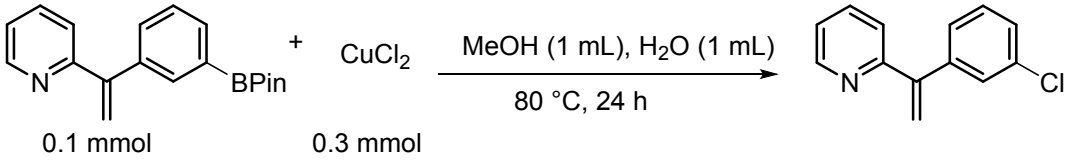
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.61 (m, 1H), 7.83 (s, 1H), 7.81 – 7.77 (m, 1H), 7.61 (td, J = 7.7, 1.8 Hz, 1H),ii 7.42 – 7.33 (m, 2H), 7.23 (d, J = 7.9 Hz, 1H), 7.19 (ddd, J = 7.5, 4.8, 1.0 Hz, 1H), 6.02 (d, J = 1.4 Hz, 1H), 5.60 (d, J = 1.4 Hz, 1H), 1.33 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.60, 149.49, 139.99, 136.37, 134.75, 134.41, 131.59, 127.74, 122.87, 122.49, 118.09, 83.94, 24.98.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.56.

HRMS: We could not observed the exact mass in HRMS in ESI (positive and negative mode) and APCI positive mode.

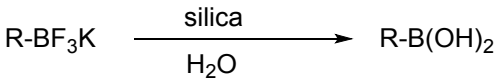
To further confirm the structure we performed halodeboronation following the reported procedure (same procedure as compound **A5**):[13]



Column: gradient from 3% - 10% EtOAc in heptane

Spectroscopic data were consistent with literature values.[2]

General Procedure for the preparation of alkyl boronic acid from alkyltrifluoroborates

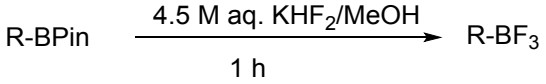


A 10 mL glass vial equipped with a magnetic stirring bar was charged with potassium alkyltrifluoroborates (0.4 mmol, 1 equiv.) and water (1 mL), followed by addition of silica (100 mg). The mixture was stirred at room temperature for 1-2 h and the progress of the reaction was monitored by ^{11}B-NMR. After completion, the mixture was diluted with EtOAc/Et_2O (10 mL) and filtered through celite or syringe filter. The organic phase was separated and the aqueous phase was extracted with EtOAc/Et_2O. The combined organic layers were dried over Na_2SO_4. The

solvent was removed in vacuum and the crude residue was used in the subsequent step without further purifications.[14]

Note: the hydrolysis of tertbutyl potassium trifluoroborate salt and α-heteroatom containing trifluoroborate salts was conducted under Ar atmosphere.

General Procedure for preparation of alkyltrifluoroborates from alkyl boronic acid pinacol esters



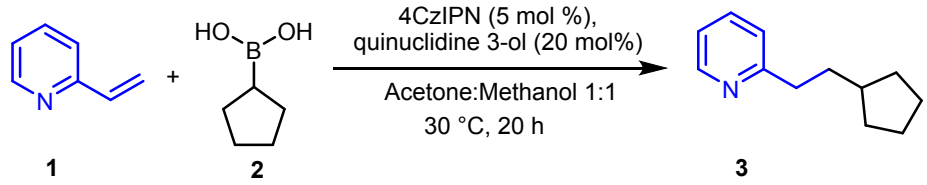
A 10 mL glass vial equipped with a magnetic stirring bar was charged with boronic ester (2 mmol, 1 equiv) and MeOH (10 mL), followed by dropwise addition of KHF_2 (2 mL of 4.5 M saturated aqueous solution, 9 mmol, 2.25 equiv). The mixture was stirred at room temperature for 1 h. Afterwards, all volatile compounds were removed in vacuum and the organic residue was re-dissolved in methanol (6 mL) followed by water (6-10 mL). All the volatile compounds were evaporated again (3 times this procedure). Then, the solid residue was triturated with dry acetone (8 mL), the liquid phase was carefully decanted, and the residual inorganic salts were washed with more acetone (3×2 mL). The filtrate was collected and concentrated *in vacuo* to give the desired trifluoroborate as a white solid.[15]

1.3. Optimization studies

General procedure for optimization: An oven-dried 10 mL glass vial equipped with a magnetic stirring bar was charged with cyclopentyl boronic acid, photocatalyst and solvent (dry solvent). The vial was closed with a silicon septum and purged with argon three times. Afterwards, the vial was charged with 2-vinyl pyridine (0.66 mmol, 1.5 equiv) and irradiated with a commercial blue LED strip (14.0 W, 450 nm) for 20 h in the aforementioned photoreactor. Progress of the reaction was monitored by TLC and GC/MS. After completion, the solution was diluted with Et_2O and transferred in a separatory funnel containing deionized water. The organic layer was separated, and aqueous layer was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuum and the yield was determined by ^{1}H-NMR using 3,4,5-trimethoxybenzaldehyde as internal standard.

*Note: Water bath temperature of the rotavapor was set at 28-35 °C. Unless otherwise noted, all the solvents used were dry.

Preliminary optimization



1 2 3

Scheme S1: preliminary optimization reaction

In view of literature[16] and our previous results obtained employing a mixture of acetone and methanol (1:1) with the addition of a Lewis base to activate boronic acids towards single electron oxidation, we performed preliminary optimization studies on the concentration of the reagents in the reaction mixture and we also determined the most suitable ratio of the starting materials, considering the possible oligomerization of 2-vinyl pyridine. We next turned our attention in finding the best conditions to perform our target reaction with the aim to avoid the use of an external Lewis base to achieve the activation.

Table S1: Preliminary optimization reactions.[a]

Entry	Lewis base	Concentration	1:2	Yield (%)[a]
1	Quinuclidine 3-ol	0.1	1.5:1	72
2	Quinuclidine 3-ol	0.05	1.5:1	70
3	Quinuclidine 3-ol	0.2	1.5:1	40
4	Quinuclidine 3-ol	0.1	3:1	67
5	Quinuclidine 3-ol	0.1	1:1.5	50
6	-	0.1	1.5:1	25

[a] Yields were determined by ^{1}H-NMRyield using 3,4,5-trimethoxybenzaldehyde as internal standard.

Solvent optimization

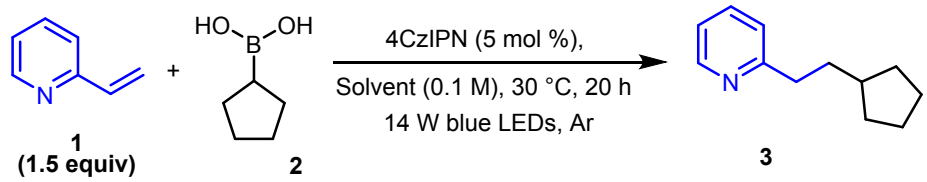


Table S2: Screening of solvents based on hydrogen-bond acceptor basicity (β) and hydrogen-bond donor(α) ability.[a]

Entry	Solvent	β[17]	α[17]	Yield (%)[b]
1	DMF	0.69	0.00	70
2	**DMA**	**0.76**	**0.00**	**80**
3	DMSO	0.76	0.00	68
4	HMPA	1.05	0.00	77
5	**NMP**	**0.77**	**0.00**	**82**
6	2-pyrrolidone	N.A	N.A	55
7	DMPU	N.A	N.A	40

[a]Reaction conditions: 1 equiv (0.22 mmol) of **2**, 1.5 equiv of **1**, 5 mol % of the photocatalyst. [b] Yields were determined by ^{1}H-NMR using 3,4,5-trimethoxybenzaldehyde as internal standard.

Photocatalyst optimization

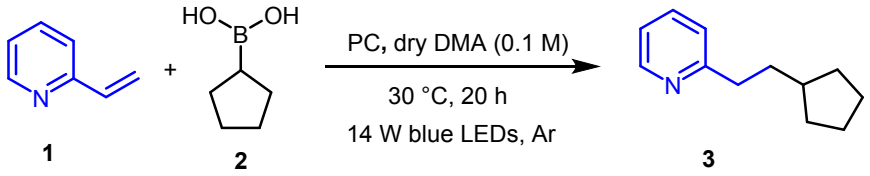
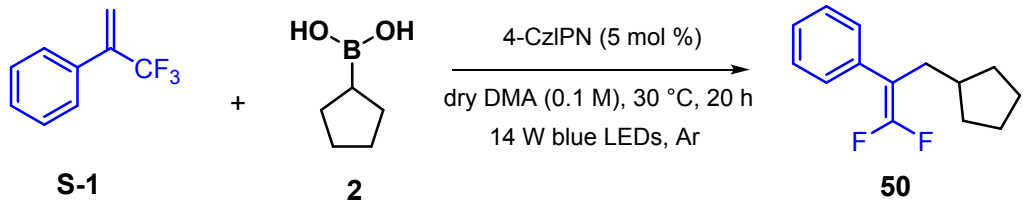


Table S3: Screening of photocatalysts.[a]

Entry	Photocatalyst	Solvent	Yield (%)[b]
1	Mes-Acr-4	DMA	0
2	4-ClCzIPN	DMA	77
3[c]	$[Ir(dtbpy)(py)_2]PF_6$	DMA	40
4[c]	$[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$	DMA	70

[a]Reaction conditions: 1 equiv (0.22 mmol) of **2**, 1.5 equiv of **1**, 5 mol% of photocatalyst. [b]Yields were determined by ^{1}H-NMR using 3,4,5-trimethoxybenzaldehyde as internal standard. [c]2 mol% of photocatalyst.

Optimization for the defluorinative alkylation reaction



S-1 2 50

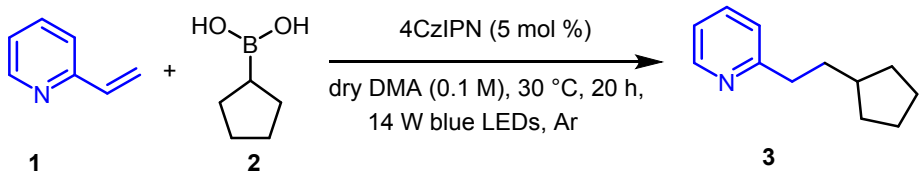
Table S4: Optimization of the reaction conditions for the defluorinative alkylation reaction.[a]

Entry	Photocatalyst	S-1:2	Additive	Concentration (M)	Yield (%)[b]
1	4CzIPN	1.5:1	-	0.1	55
2	4CzIPN	1:1.5	-	0.1	75
3	4CzIPN	1:1.5	Mol. sieves	0.1	76

[a]Reaction conditions: 5 mol % of photocatalyst. [b]Yield were determined by ^{1}H-NMR using dibromomethane.

1.4. Mechanistic investigations

Control experiments: To explain the mechanism of the alkylation reaction, control experiments were performed. The results of the variation of the optimal reaction conditions are presented in Table S5. In the absence of light and photocatalyst (**Entry 2,3**), the product was not detected; in the absence of an oxygen free atmosphere (**Entry 4**), the yield was consistently decreased. This result can be accounted for the involvement of oxygen in quenching the excited state of the photocatalyst. These results confirm the photocatalyzed mechanism of the presented method. The use of MIDA boronate did not result in any desired product formation. This result highlights the necessity of both hydrogen bonding and Lewis acid-base interaction, both impossible with a MIDA boronate (**Entry 6**). Moreover, the reaction was not found to be sensitive to the presence of water, allowing to perform this reaction in biocompatible conditions (**Entry 7**).



1 2 3

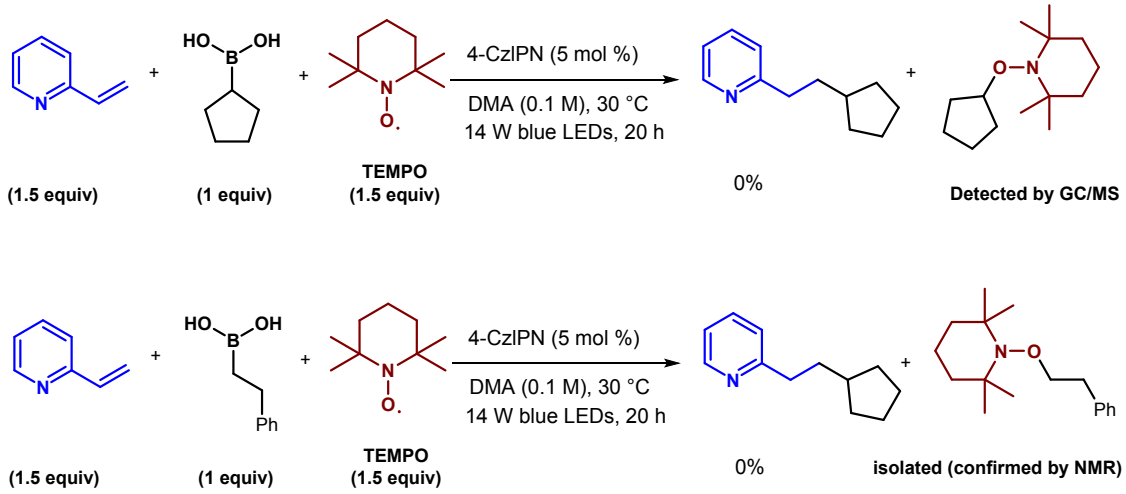
Table S5: Control experiments.

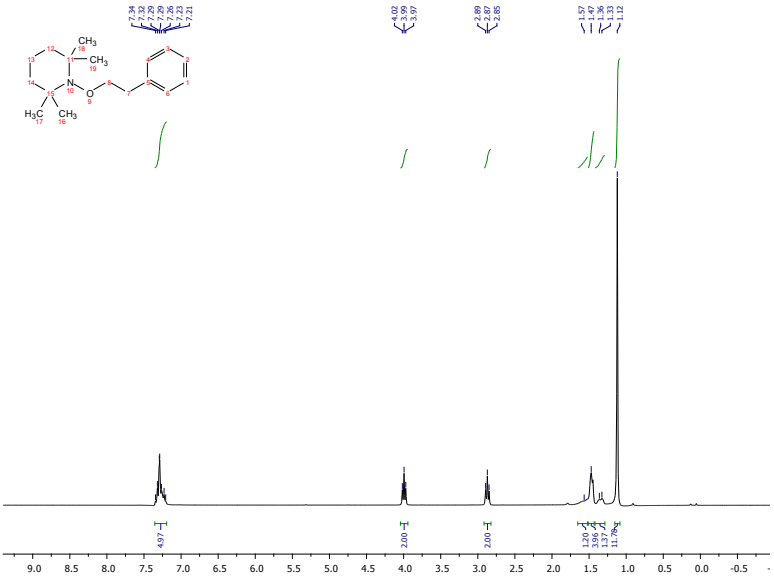
Entry	Deviation from standard conditions[a]	Yield (%)[b]

1	none	80 (77)
2	No PC	-
3	No light	-
4	Under air	30
5	0.5 M DMA	37
6	Cyclohexylboronic acid MIDA	0
7[c]	H_2O:DMA (9:1)	68
8	1 equiv of DMAP	40

[a]Reaction conditions: 1 equiv (0.22 mmol) of **2**, 1.5 equiv of **1**, 5 mol% of photocatalyst in DMA (0.1 M). [b]Yields were determined by ^{1}H-NMR using 3,4,5-trimethoxybenzaldehyde as internal standard. Isolated yields are in parentheses. [c]Solubility of 4CzIPN is poor and therefore may be the cause of the lower yield.

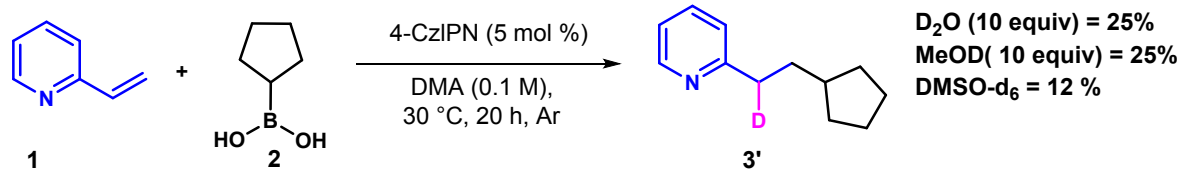
Radical inhibition experiment: Adding a radical quencher (TEMPO) to the reaction mixture, an adduct between cyclohexane ring and TEMPO itself was detected by GC-MS. Moreover, the adduct between TEMPO and phenylethyl radical (deriving from phenylethyl boronic acid) was isolated (48% yield) and characterized by NMR. These results support the radical based mechanism (Scheme S2).





Scheme S2: Radical inhibition experiment: reaction conducted in the presence of a radical scavenger.

Deuterium-labelling experiment: In the presence of D_2O, deuterium incorporation is obtained (25%), substantiating the hypothesis of a last protonation step in the redox-neutral reaction mechanism (Scheme S3). The low deuterium incorporation in the final product could be due to the presence of active hydrogens derived from DMA-BA intermediate. However, this low amount of deuteration in the presence of D_2O also excludes the *in-situ* formation of hydroxide ion (OH^-), which could interact with BA and favour the boronate ion formation.[18]



Scheme S3: Deuterium labelling experiment

Light-dark experiment: In the absence of light no product formation was detected. This result suggests the fundamental role of light in the reaction mechanism, but it cannot completely exclude a radical chain mechanism (Figure S2).

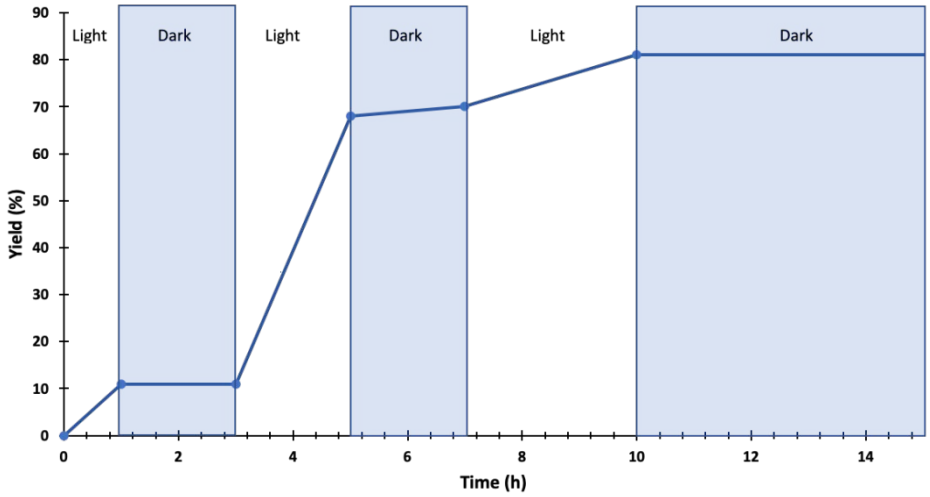


Figure S2: Results of the light-dark experiment.

Stern-Volmer quenching experiment: The experiment was performed on a fluorescence spectrophotometer (FLS 920, Edinburgh Instruments, Photonic division). In a typical experiment, to a 0.1 mM solution of 4CzIPN in ACN, an appropriate amount of quencher was added in a 1.0 cm quartz cuvette. The solutions were irradiated at 400 nm and emission was measured at 540 nm. The relative intensity I_0/I was calculated as a function of quencher concentration, where I_0 is the luminescence intensity in the absence of quencher, while I is the intensity in the presence of the quencher. Before each measurement, the solutions were degassed and kept under nitrogen atmosphere (Figure S3).

Figure S3: Preparation of the sample under inert atmosphere using an in-house made silicon cap.

The Stern-Volmer experiment demonstrates that only a mixture of boronic acid and DMA is able to quench the excited state of 4CzIPN, substantiating the hypothesis that only the interaction between boronic acids and DMA gives rise to a redox-active substrate (Figure S4). Indeed, neither

boronic acid nor DMA independently are able to quench the excited state of the photocatalyst (Figure S5 and S6).

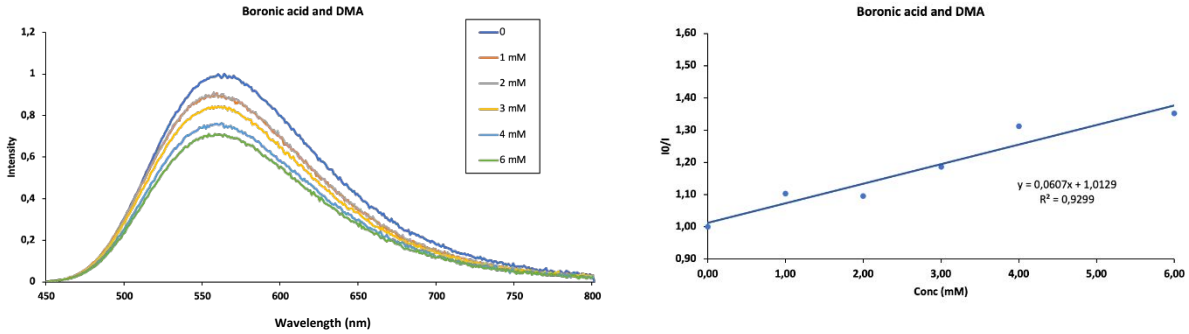


Figure S4: Fluorescence quenching and Stern-Volmer plot of 4CzIPN in the presence of variable concentrations of cyclohexyl boronic acid and DMA (3M).

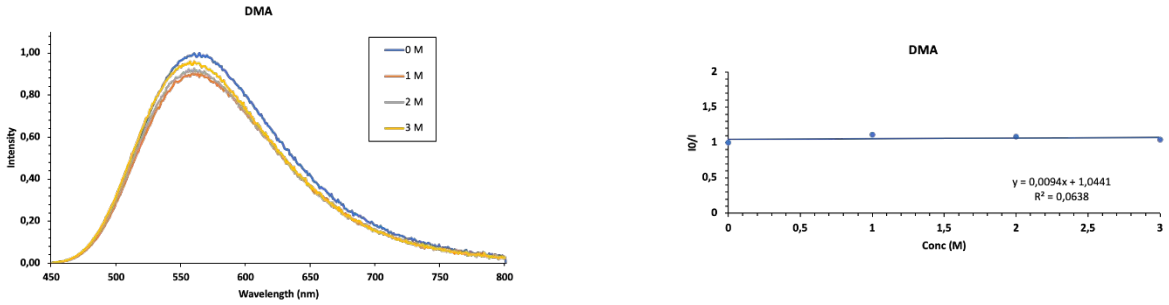


Figure S5: Fluorescence quenching and Stern-Volmer plot of 4CzIPN in the presence of variable concentrations of DMA.

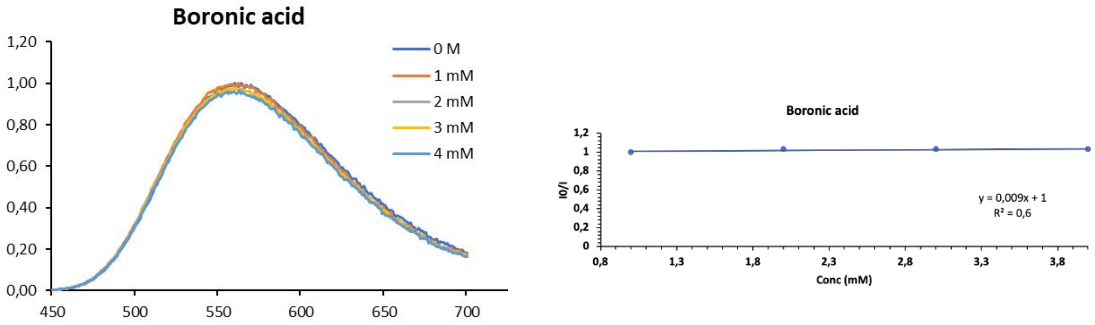


Figure S6: Fluorescence quenching and Stern-Volmer plot in the presence of cyclohexyl boronic acid.

NMR experiment: To demonstrate the interaction between boronic acids and DMA, ^{1}H-NMR spectra of a mixture of **phenylethyl boronic acid** (0.014 M in $CDCl_3$) and different concentrations of **DMA** were performed at 298.2 K. Increasing the concentration of DMA, a downfield shift of hydrogens (B-O-H) could be observed as a result of the formation of hydrogen bonds between **phenylethyl boronic acid** and **DMA** (Figure S7). Due to the presence of two different species of BA in $CDCl_3$, the change in the chemical shift of the -CH_2- (next to boron center) proton upon interaction with DMA could not be analyzed. In order to confirm the chemical shift of this protons, we ran the experiment in acetone-d_6. As expected, we can see a slight upfield shift (Figure S8).

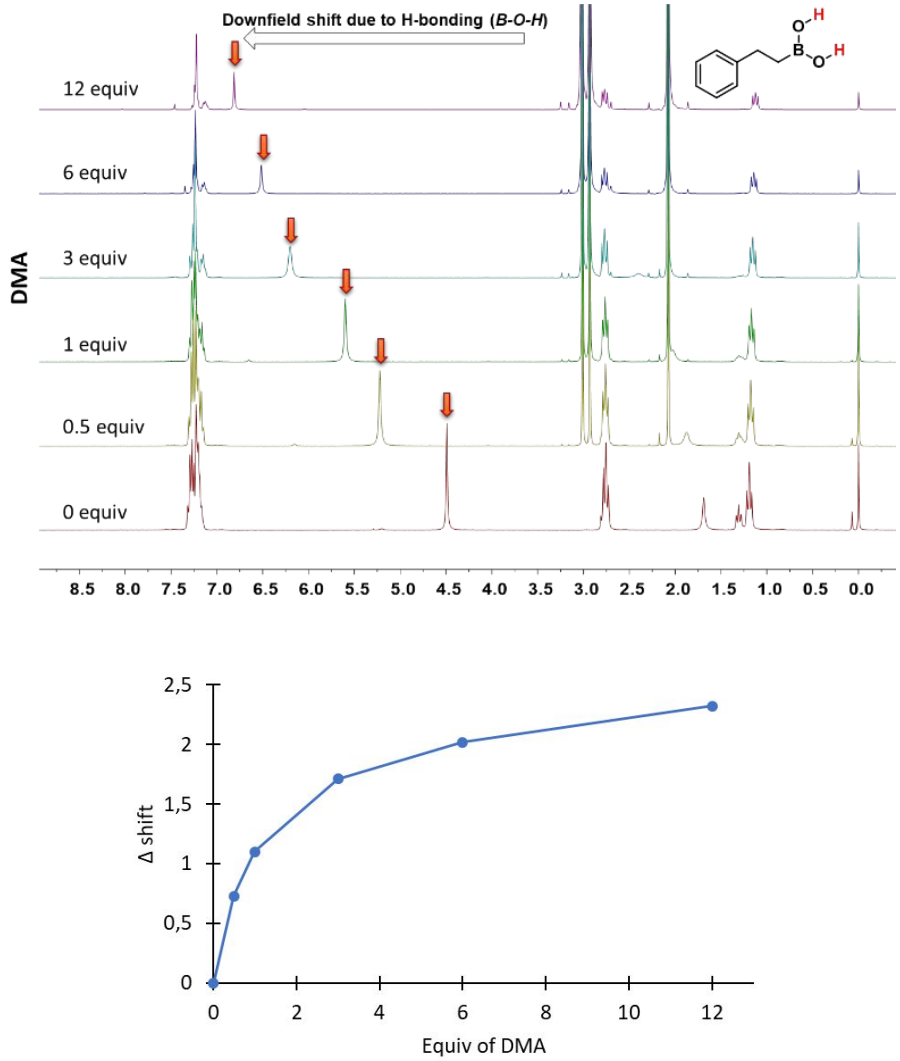


Figure S7: ^{1}H-NMR titration curve of phenyl ethyl boronic acid with DMA in $CDCl_3$ (based on the shift of B-OH bond).

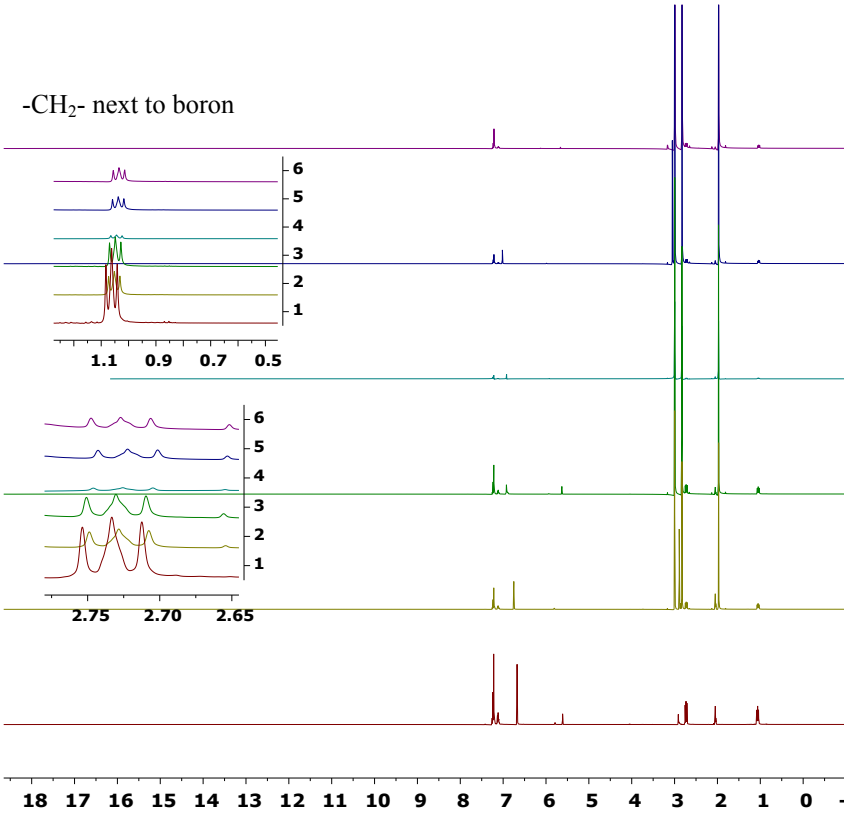


Figure S8: ^{1}H-NMR spectrum of phenyl ethyl boronic acid in the presence of increasing concentrations of DMA in acetone-d_6.

To further establish the hydrogen bond interaction, ^{31}P-NMR spectrum of a mixture of **phenylethyl boronic acid** (0.01 M in CD_2Cl_2) and **HMPA** (0.01 M in CD_2Cl_2) was performed. HMPA showed an appreciable shift in the presence of a boronic acid, as shown in Figure S9. The shift observed in the presence of BA also supports the hypothesis of contribution of H-bonding and Lewis acid-base interaction.

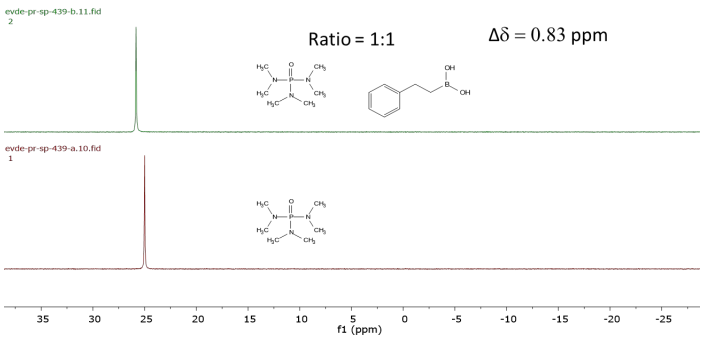


Figure S9: ^{31}P-NMR spectrum of HMPA in the presence of phenyl ethyl BA.

Boronic acid speciation: Boronic acids are prone to form boroxine under anhydrous conditions or in the presence of dehydrating agents.[19] In order to confirm the precentage of boroxine and boronic acid in a commerical phenyl ethyl boronic acid sample, we performed ^{1}H experiment in DMSO-d_6 at 298.2 K. We could easily see the –OH peak (2 protons, Figure S10) deriving from free boronic acid without any other peaks from boroxine. Nevertheless, the speciation of boronic acids during the course of the photocatalytic cycle cannot be predicted, as a result of the generation of anionic species (fluorine and tosyl anions), which can be involved, to a minor extent, in the activation of boronic acids.[16] Despite this possibility, the major activation pathway is ruled by the interaction between DMA and free boronic acids.

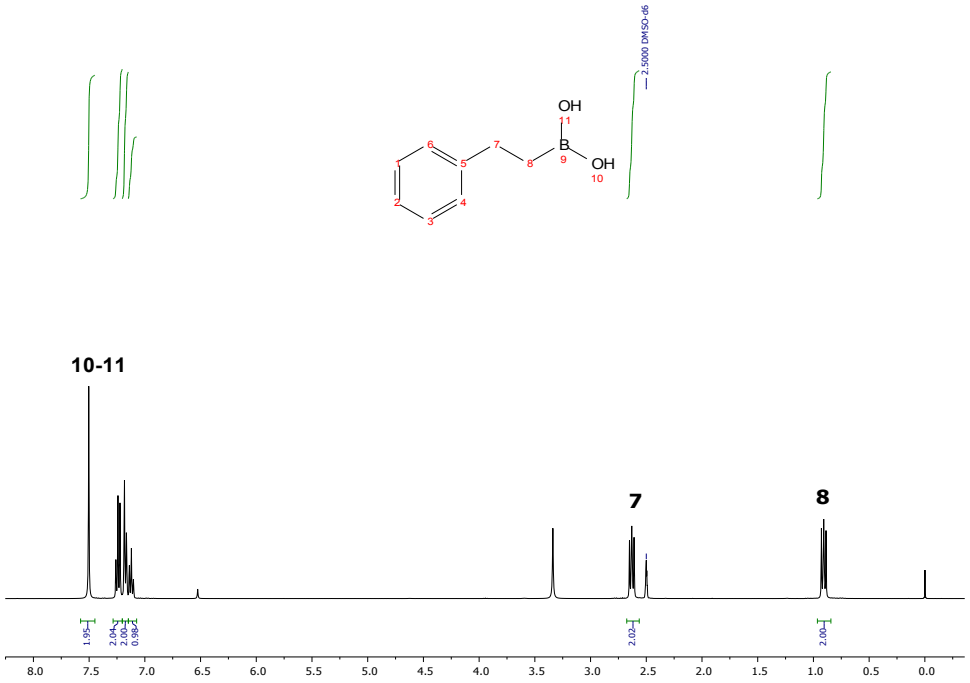


Figure S10: ^{1}H-NMR spectrum of phenyl ethyl BA in DMSO-d_6.

Job's plot: Various solutions of phenyl ethyl boronic acid and DMA in acetone-d_6 were prepared, with the sum of both concentrations at a constant value of c_{tot} = 0.13 mol/L. ^{1}H NMR of the solutions was recorded at 298 K on a Bruker Avance 300 MHz spectrometer. The result (Figure S11) shows a maximum at χ = 0.3, which indicates a 2.3:1 stoichiometry of the intermediate obtained through the combination of strong hydrogen bonds and weaker and transient Lewis acid-

base interactions between the two species present in solution (as already confirmed through ^{31}P NMR, Figure S9).

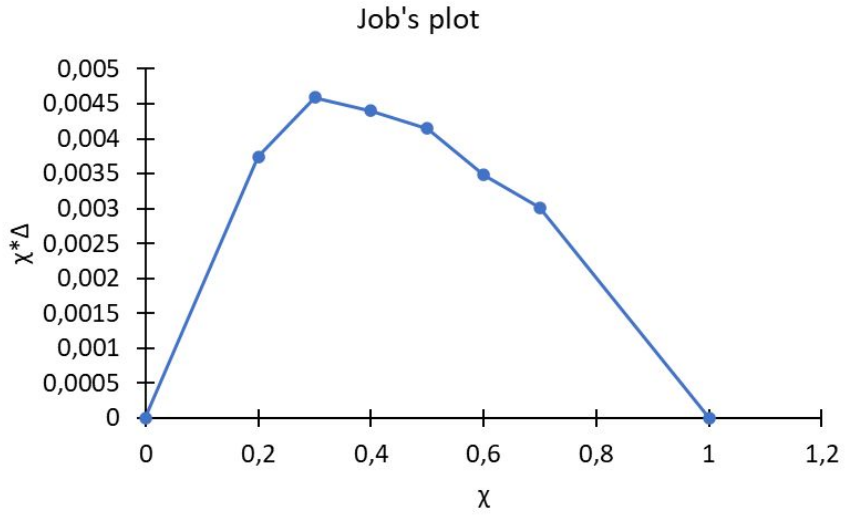


Figure S11: Job's plot Job plot analysis ($\chi^*\Delta\delta$ as a function of χ). χ is the molar fraction of phenyl ethyl boronic acid

Cyclic voltammetry measurements: In light of the results of ^1H-NMR experiments, we performed cyclic voltammetry experiments to understand the effect of the interaction between boronic acids and DMA on the oxidation potential of these species.

Procedure: The experiments were conducted using a cyclic potentiometer (Metrohm PGSTAT20 potentiostat/ galvanostat) with a glassy carbon working electrode, a Pt counter electrode and an Ag/AgCl reference electrode [referenced to SCE using ferrocene (Fc) as an internal standard (0.42 V *vs*. SCE)].[20] In the standard procedure, 0.02 mmol of substrate were dissolved in 10 mL of a 0.1 M $[N(Bu)_4]PF_6$ electrolyte solution in degassed MeCN. The reactor was sealed with a rubber septum and purged with nitrogen. Each measurement was conducted at 100 mV/s at room temperature under nitrogen atmosphere without stirring.

At first, the redox potentials of boronic acid **2** and DMA were measured. The observed oxidation peaks (2.24 V *vs* SCE for phenyl ethyl boronic acid and 2.01 V *vs* SCE for DMA) lie outside the redox window of 4CzIPN ($E_{1/2}$ (P^*/P^-) = +1.43, $E_{1/2}$ (P/P^-) = -1.24 *vs* SCE), (Figure S13).

The cyclic voltammogram of a mixture of boronic acid **2** and DMA (1:4) was then measured. In the voltammogram, beside the peaks of the boronic acid and DMA, it is possible to observe a new local maximum, which is related to the species formed through the interaction between boronic acid and DMA in the mixture (Figure S12).

To correctly define the oxidation potential of the new arising oxidizable species, in our case the Nernst equation could not be employed, since an irreversible cyclic voltammogram was obtained. This result can be accounted for the reactivity of the oxidized species, which undergoes degradation. To estimate the value of $E^0_{1/2}$, the half peak potential $E_{p/2}$ (which corresponds to the potential at half the maximum of the local maximum current in the cyclic voltammogram) was calculated (Equation S1).

$$f\ (Ep/2\ ) = C\mathrm{max}/2 \qquad \textbf{[Equation S1]}$$

In the case of boronic acid and DMA, the half peak potential value was found to be 1.13 V *vs* SCE. This species can therefore quench the excited state of 4CzIPN, as the value found lies in the redox window of the PC. The result obtained proves that DMA can activate boronic acids towards oxidation.

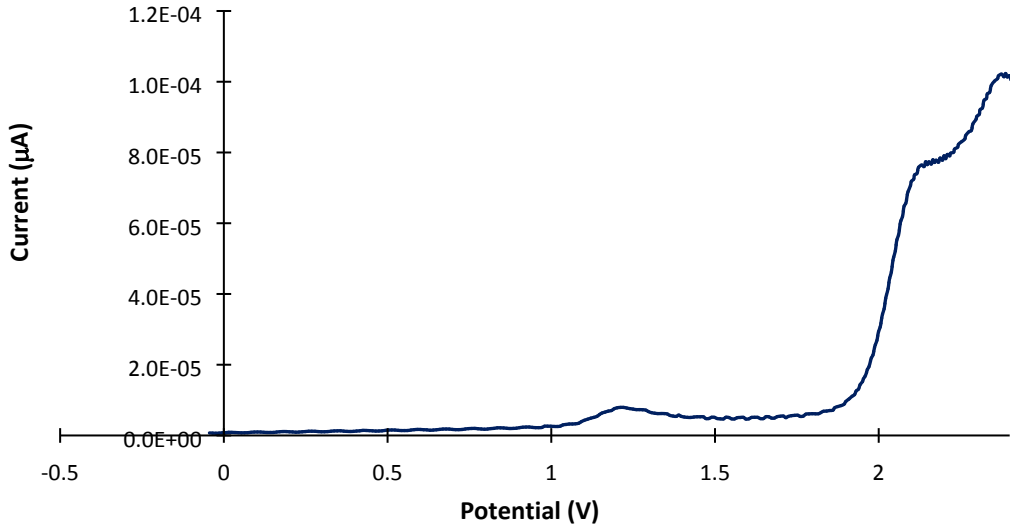


Figure S12: Cyclic voltammogram of boronic acid **2** in the presence of DMA.

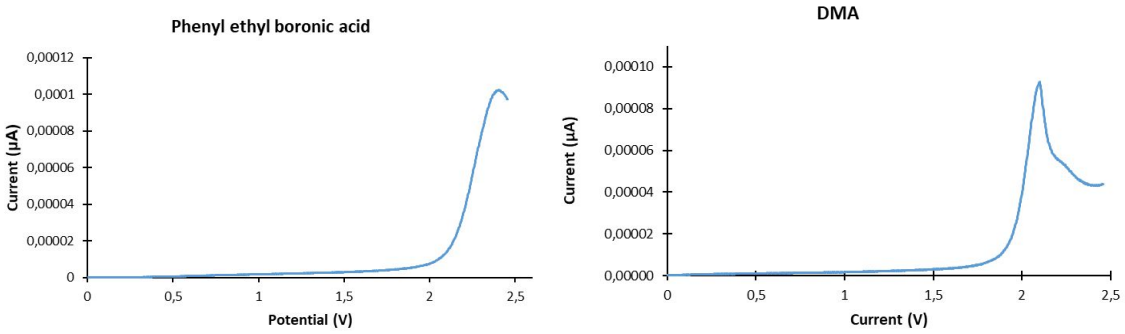


Figure S13: Cyclic voltammograms of boronic acid **2** and of DMA.

Competition experiment: To define the reaction kinetics and selectivity in the presence of two boron species with similar redox values, a competition experiment was performed. In the presence of cyclopentyl boronic acid (1 equiv) and cyclohexyl boronic acid pinacol ester (1 equiv), it was observed that the activation of boronic acid by DMA was faster and afforded the alkylated product as major product. Indeed, DMA is able to activate boronic acids towards single electron transfer (SET), but the same mode of activation of boronic esters is slower, as illustrated in Figure S14. This result explains the possibility to achieve the selective activation of boronic acids in the presence of boronic esters, which show similar chemical features in terms of oxidation potential. Nevertheless, the solvent is able to interact with boronic acids in a more efficient manner (through hydrogen bonding and Lewis acid/base interaction) in the presence of both the species.

To further exclude the steric effect of pinacol boronic esters, we subjected cyclopentyl boronic acid methyl ester, less sterically hindered than the pinacol counterpart, to the same reaction conditions. We could not observe a high product formation. This substantiates our hypothesis of a greater contribution of electronic effects over steric effects (Figure S15).

Intrigued by the possibility to obtain product formation from boronic esters as well (in the absence of boronic acids), we performed alkylation reaction using different boronic esters as radical source. Unfortunately, we could not find a reactivity trend to explain the reactivity of secondary boronic esters. Further studies are currently undergoing in our laboratory (Figure S16).

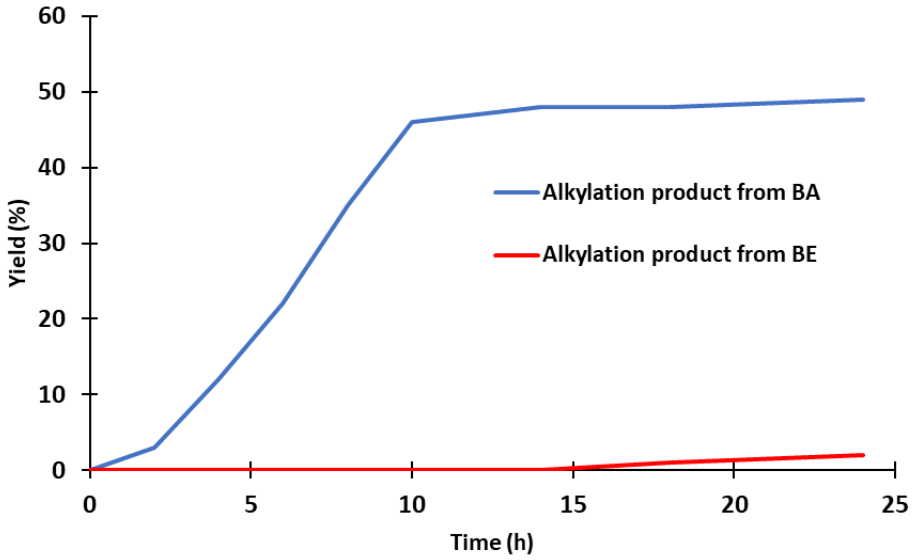


Figure S14: Competitive experiment in the presence of cyclopentyl boronic acid (1 equiv) and cyclohexyl boronic ester (1 equiv), under the general reaction conditions (1 equiv of 2-vinyl pyridine, 5 mol% of 4CzIPN, 0.1 M in DMA under Ar atmosphere).

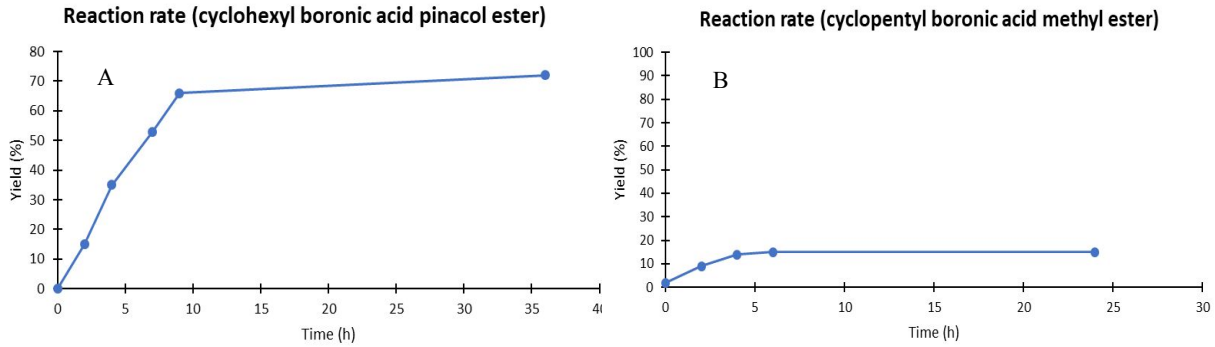


Figure S15: Reaction rate of cyclohexyl boronic acid pinacol ester (A) and cyclopentyl boronic acid methyl ester (B) under the general reaction conditions (1.5 equiv of 1-(trifluoromethyl)-4-vinylbenzene, 5 mol% of 4CzIPN, 0.1 M in DMA under Ar atmosphere), yields were measured by GC-MS.

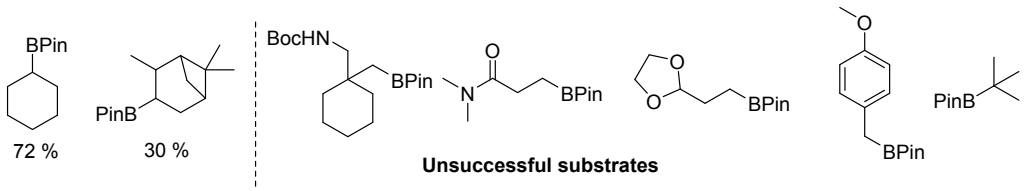
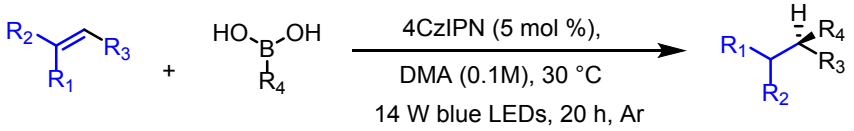


Figure S16: Evaluation of the reactivity of boronic acid pinacol esters under our optimized conditions, using 2-vinyl pyridine as radical acceptor.

1.5. General procedure for the alkylation of electron deficient alkenes (GP1)



An oven-dried 10 mL glass vial equipped with a magnetic stirring bar was charged with alkyl boronic acid (1 equiv, 0.44 mmol), photoredox catalyst (4CzIPN, 5 mol%) and DMA (0.1 M). The vial was closed with a silicon septum and purged with argon three times. The vial was then charged with the electron deficient alkene (1.5 equiv, 0.66 mmol) and irradiated with a commercial blue LED strip (14 W, 450 nm) for 20 h in the aforementioned photoreactor. The progress of the reaction was monitored by TLC and GC/MS. After completion, the solution was diluted with Et_2O and transferred in a separatory funnel containing deionized water. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4. Purification was performed by SiO_2 column chromatography.

For the pyridine containing compounds: before the purification, silica was neutralized with a 2% Et_3N solution in heptane.

TLC: 20% EtOAc in heptane (R_f: 0.45)

Column: gradient 5% to 15 % EtOAc in heptane

***Note**: Water bath temperature of the rotavapor was set at 28 °C.

General procedure for continuous-flow experiments

An oven-dried 10 mL glass vial equipped with a stirring bar was charged with alkyl boronic acid (1 equiv), photoredox catalyst (4CzIPN, 5 mol%) and a mixture of ACN and DMA (4:1, 0.1 M). The vial was closed with a silicon septum and purged with argon three times. The vial was then charged with the electron deficient alkene (1.5 equiv). The resulting clear yellow solution was then pumped through a *10 mL volume reactor* at the desired flow rate, keeping the temperature set at 20 °C. Once the solution had been fully taken up by the pump, the input was changed to ACN/DMA solvent to push the reaction

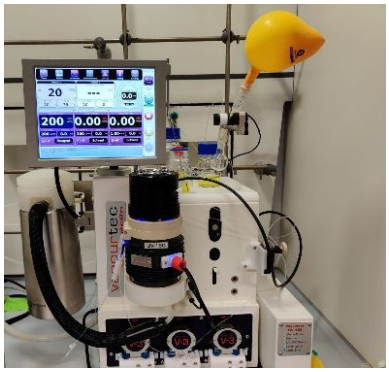


Figure S17: Vapourtec E-series photoreator; reaction setup.

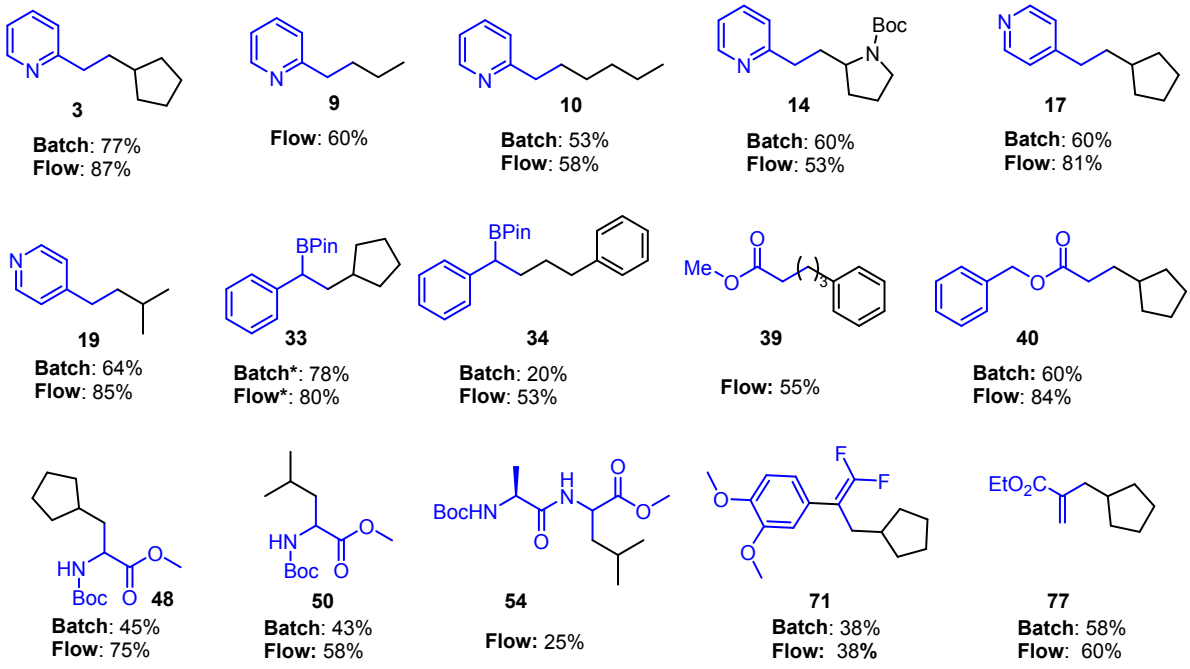
mixture through the reactor. The crude reaction mixture was collected in a round bottom flask and analyzed through GC/MS or NMR.

Table S6: Comparison between batch and flow results.

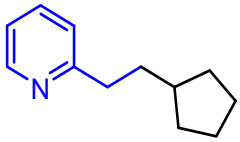
Scale (mmol)	Concentration (M)	Mode Batch/flow[a]	Solvent (V/V)	Flow rate (mL/min)	Isolated yield (%)	Production (mmol/h)
0.4	0.1	batch	DMA	NA	77	0.015
1	0.1	batch	DMA	NA	68	0.034
0.4	0.1	flow	DMA	0.2	45	0.22
0.4	0.1	flow	DMA/ACN 1:4	0.2	87	0.42
2	0.1	flow 2 run	DMA/ACN 1:4	0.2	68	0.816

[a]Power = 24 W, Volume of reactor = 10 mL

Substrate Scope in Flow



2-(2-cyclopentylethyl)pyridine (3)



Compound **3** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 2-10 % EtOAc/Heptane

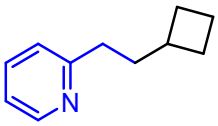
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, J = 5.1, 1.8 Hz, 1H), 7.56 (td, J = 7.7, 1.9 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 7.07 (dd, J = 7.5, 4.9 Hz, 1H), 2.82 – 2.76 (m, 2H), 1.84 – 1.67 (m, 5H), 1.66 – 1.51 (m, 2H), 1.50 (dq, J = 11.7, 6.7, 5.2 Hz, 2H), 1.19 – 1.09 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.68, 149.16, 136.22, 122.63, 120.81, 39.95, 37.71, 36.39, 32.64, 25.22.

IR (neat, ν/cm^{-1}) 2975, 1684, 1395, 1358, 1166, 1143.

HRMS (ESI$^+$): $[M+H]^+$cal'd for $C_{12}H_{18}N$:176.14336 found: 176.1437

2-(2-cyclobutylethyl)pyridine (4)



Compound **4** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 2-10 % EtOAc/Heptane

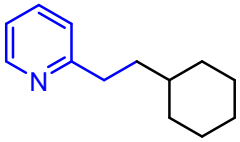
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, J = 4.0 Hz, 1H), 7.60 – 7.51 (m, 1H), 7.11 (d, J = 8.0 Hz, 2H), 2.74 – 2.64 (m, 2H), 2.27 (d, J = 2.9 Hz, 1H), 2.12 – 1.96 (m, 2H), 1.81 (q, J = 7.5 Hz, 4H), 1.70 – 1.54 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.57, 149.27, 136.29, 122.78, 120.91, 37.20, 36.22, 35.94, 28.30, 18.53.

IR (neat, ν/cm^{-1}) 2925, 2853, 1591, 1473, 1433, 747.

HRMS(ESI$^+$): $[M+H]^+$ cal'd for $C_{11}H_{16}N$: 162.1277, found: 162.1278

2-(2-cyclohexylethyl)pyridine (5)[21]



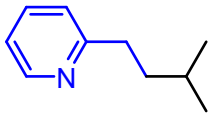
Compound **5** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 2-10 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 4.8 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.14 – 7.08 (m, 1H), 7.10 – 7.01 (m, 1H), 2.80 – 2.74 (m, 2H), 1.78 (d, J = 13.1 Hz, 2H), 1.74 – 1.58 (m, 5H), 1.28 – 1.12 (m, 4H), 1.00 – 0.89 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.89, 149.19, 136.21, 122.61, 120.77, 37.66, 37.57, 35.91, 33.27, 26.67, 26.35. Spectroscopic data were consistent with literature values.

2-isopentylpyridine (6)[22]

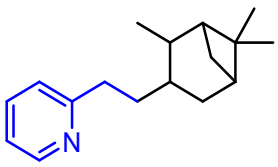


Compound **6** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 2-10 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (d, J = 4.2 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.10-7.06 (m, 2H), 2.83 – 2.76 (m, 2H), 1.63-1.59 (m, 3H), 0.95 (d, J = 5.2 Hz, 6H). Spectroscopic data were consistent with literature values.

2-(2-(2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)ethyl)pyridine (7)



Compound **7** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 2-12 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 – 8.49 (m, 1H), 7.57 (td, J = 7.7, 1.8 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 7.10 – 7.04 (m, 1H), 2.89 (ddd, J = 13.6, 11.1, 4.6 Hz, 1H), 2.74 (ddd, J = 13.6, 10.6, 6.0

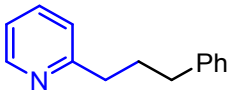
Hz, 1H), 2.32 – 2.17 (m, 2H), 1.95 (m, 2H), 1.76 (dd, *J* = 9.0, 3.9 Hz, 1H), 1.73 – 1.52 (m, 5H), 1.19 (s, 3H), 1.03 – 0.98 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.85, 149.35, 136.33, 122.71, 120.93, 48.44, 43.88, 42.16, 41.46, 38.93, 37.01, 36.63, 34.84, 34.18, 28.25, 23.12, 21.81.

IR (neat, ν/cm^{-1}) 2902, 1594, 1568, 1472, 1452, 1433, 1372, 1315, 1146, 746

HRMS(ESI$^+$)[M+H]$^+$ cal'd for $C_{17}H_{25}N$: 244.2059, found : 244.2068

2-(3-phenylpropyl)pyridine (8)[23]



Compound **8** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

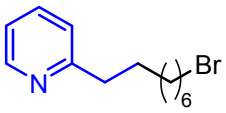
Column Chromatography : Silica, gradient 5-20 % EtOAc/*iso*-Hexane

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.50 (m, 1H), 7.63 – 7.58 (m, 1H), 7.29 (m, 2H), 7.24 – 7.16 (m, 3H), 7.16 – 7.10 (m, 2H), 2.85 (m, 2H), 2.74 – 2.68 (m, 2H), 2.15 – 1.99 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.02, 149.25, 142.23, 136.54, 128.58, 128.42, 125.88, 122.96, 121.16, 77.48, 77.16, 76.84, 37.91, 35.66, 31.58. Spectroscopic data were consistent with literature values.

Note: Compound 8 is smelly; all the work-up process should be done under proper ventilated hood.

2-(8-bromooctyl)pyridine (9)[24]

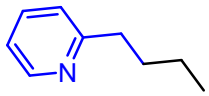


Compound **9** was prepared according to the general procedure (GP1) and isolated as a clear oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.8 Hz, 1H), 7.56 (td, *J* = 7.6, 1.7 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.07 (dd, *J* = 7.4, 5.0 Hz, 1H), 3.38 (t, *J* = 6.9 Hz, 2H), 2.81 – 2.70 (m, 2H), 1.87 – 1.78 (m, 2H), 1.70 (dd, *J* = 15.0, 7.4 Hz, 2H), 1.43 – 1.32 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.52, 149.25, 136.47, 122.86, 121.04, 77.16, 38.49, 34.18, 32.95, 29.98, 29.41, 28.79, 28.28. Spectroscopic data were consistent with literature values.

2-butylpyridine (10)[25]

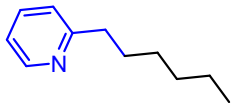


Compound **10** was prepared according to the general flow procedure and isolated as a clear oil.

Column Chromatography : Silica, gradient 0-10 % EtOAc/*iso*-Hexane

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.5 Hz, 1H), 7.56 (dt, *J* = 7.7, 3.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.08 (dd, *J* = 7.2, 5.1 Hz, 1H), 2.81 – 2.75 (m, 2H), 1.75 – 1.66 (m, 2H), 1.43 – 1.32 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). Spectroscopic data were consistent with literature values.

2-hexylpyridine (11)[26]



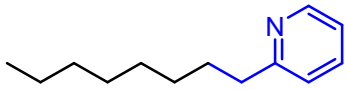
Compound **11** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 5-20 % Et_2O/Pentane (after neutralizing silica with 2% Et_3N)

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.52 – 8.49 (m, 1H), 7.56 (td, *J* = 7.7, 1.8 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.07 (dd, *J* = 7.4, 5.0 Hz, 1H), 2.79 – 2.74 (m, 2H), 1.70 (q, *J* = 7.6 Hz, 2H), 1.37 – 1.26 (m, 6H), 0.91 – 0.82 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* 162.67, 149.30, 136.30, 122.77, 120.93, 38.59, 31.83, 30.02, 29.21, 22.70, 14.19. Spectroscopic data were consistent with literature values.

2-octylpyridine (12)[27]



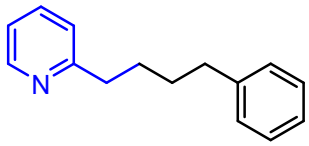
Compound **12** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 5-20 % Et_2O/Pentane (after neutralizing silica with 2% Et_3N)

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 8.51 (d, *J* = 4.7 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.16 – 6.97 (m, 2H), 2.77 (t, *J* = 7.8 Hz, 2H), 1.72 (p, *J* = 7.3 Hz, 2H), 1.41 – 1.18 (m, 10H), 0.86 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.36, 148.97, 136.00, 122.47, 120.62, 38.27, 31.66, 29.74, 29.27, 29.23, 29.03, 22.46, 13.90. Spectroscopic data were consistent with literature values.

2-(4-phenylbutyl)pyridine(13)[28]



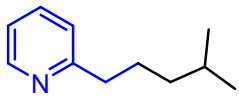
Compound **13** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 2-10 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (ddd, J = 4.9, 1.9, 1.0 Hz, 1H), 7.57 (td, J = 7.6, 1.9 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.16 (td, J = 5.3, 4.9, 2.3 Hz, 3H), 7.13 – 7.06 (m, 2H), 2.84 – 2.78 (m, 2H), 2.69 – 2.61 (m, 2H), 1.84 – 1.75 (m, 2H), 1.73 – 1.64 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.30, 149.36, 142.65, 136.38, 128.53, 128.39, 125.78, 122.84, 121.05, 38.40, 35.95, 31.33, 29.66. Spectroscopic data were consistent with literature values.

2-(4-methylpentyl)pyridine(14)[29]



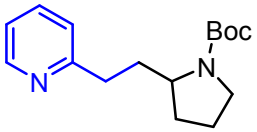
Compound **14** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 2-10 % EtOAc/Heptane (after neutralizing silica with 2% Et_3N)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 4.0 Hz, 1H), 7.57 (td, J = 7.7, 1.9 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 7.08 (ddd, J = 7.4, 4.9, 1.0 Hz, 1H), 2.78 – 2.72 (m, 2H), 1.77 – 1.67 (m, 2H), 1.57 (dp, J = 13.3, 6.7 Hz, 1H), 1.28 – 1.20 (m, 2H), 0.88 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.67, 149.31, 136.33, 122.79, 120.96, 38.85, 28.06, 27.95, 22.72. Spectroscopic data were consistent with literature values.

tert-butyl 2-(2-(pyridin-2-yl)ethyl)pyrrolidine-1-carboxylate (15)[30]

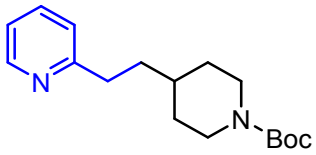


Compound **15** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 5-25 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (d, J = 3.0 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.16 – 7.00 (m, 2H), 3.99 – 3.74 (m, 1H), 3.41-3.28 (m, 2H), 2.86 – 2.71 (m, 2H), 2.02-1.98 (m, 1H), 1.96-1.87 (m, 2H), 1.82-1.72 (m, 3H), 1.44 (s, 9H). Spectroscopic data were consistent with literature values.

tert-butyl 4-(2-(pyridin-2-yl)ethyl)piperidine-1-carboxylate (16)[31]

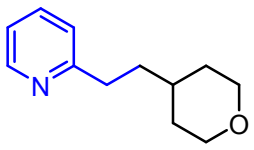


Compound **16** was prepared according to the general procedure (GP1) and could not be isolated as a pure compound because of the presence of the byproducts arising from the decomposition of the photocatalyst (4CzIPN). Yield was determined by ^{1}HNMR using dibromomethane as an internal standard.

Column Chromatography: Silica, 50 % DCM/ Heptane to remove the catalyst then gradient 10-35 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (d, J = 4.4 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.08 (m, 2H), 3.88 (br, 2H), 2.82 – 2.73 (m, 2H), 2.64 (m, 2H), 1.74 – 1.60 (m, 4H), 1.42 (s, 10H), 1.15 – 1.06 (m, 2H). Spectroscopic data were consistent with literature values.

2-(2-(tetrahydro-2H-pyran-4-yl)ethyl)pyridine (17)[31]

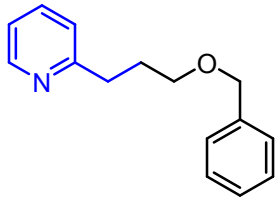


Compound **17** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography: Silica, gradient 10-33 % EtOAc/Heptane

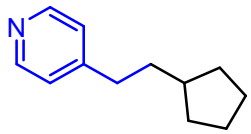
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 4.8 Hz, 1H), 7.57 (dd, J = 10.6, 4.7 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 7.09 – 7.05 (m, 1H), 3.97 – 3.90 (m, 2H), 3.34 (t, J = 11.7 Hz, 2H), 2.79 (dd, J = 8.8, 7.4 Hz, 2H), 1.72 – 1.59 (m, 4H), 1.52 (tt, J = 7.6, 5.2 Hz, 1H), 1.32 (m, 2H). Spectroscopic data were consistent with literature values.

2-(3-(benzyloxy)propyl)pyridine (18)[32]



Compound **18** was prepared according to the general procedure (GP1) and isolated as a brown oil.
^{1}H NMR (300 MHz, CDCl3) δ 8.52 (d, J = 4.4 Hz, 1H), 7.55 (td, J = 7.7, 1.4 Hz, 1H), 7.33 (m, 4H), 7.29 – 7.24 (m, 1H), 7.12 (d, J = 7.4 Hz, 1H), 7.06 (dd, J = 11.9, 5.1 Hz, 1H), 4.50 (s, 2H), 3.52 (t, J = 6.3 Hz, 2H), 2.89 (t, J = 7.7 Hz, 2H), 2.13 – 1.83 (m, 2H). Spectroscopic data were consistent with literature values.

4-(2-cyclopentylethyl)pyridine (19)



Compound **19** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 2-10 % EtOAc/Heptane

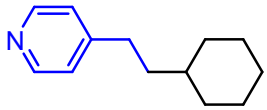
^{1}H NMR (400 MHz, Chloroform-d) δ 8.47 (d, J = 5.73, 2H), 7.10 (d, J = 5.73 Hz, 2H), 2.60 (t, J = 8.07 Hz, 2H), 1.77-1.70 (m, 3H), 1.65-1.57 (m, 4H), 1.54-1.49 (m, 2H), 1.14-1.10 (m, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 151.94, 149.60, 123.90, 39.59, 36.86, 34.48, 32.60, 25.20.

IR (neat, ν/cm^{-1}) 2975, 2873, 1685, 1395, 1358, 1166, 1143, 729.

HRMS(ESI^+): [M+H] cal'd for $C_{12}H_{18}$: 176.1433, found : 176.1437

4-(2-cyclohexylethyl)pyridine (20)[21]



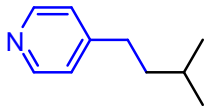
Compound **20** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 2-10 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (d, *J*=5.91 Hz, 2H), 7.10 (d, *J*=5.93, 2H), 2.60 (t, *J*=8.2 Hz, 2H), 1.79 – 1.68 (m, 6H), 1.54 – 1.46 (m, 2H), 1-26-1.28 (m, 1H), 1.22-1.15 (m, 2H), 0.99 – 0.87 (m, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 152.27, 149.74, 124.02, 38.24, 37.38, 33.35, 32.74, 26.73, 26.40, 0.14. Spectroscopic data were consistent with literature values.

4-isopentylpyridine (21)[22]

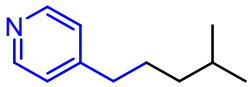


Compound **21** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 2-10 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (d, *J*=5.91 Hz, 2H), 7.10 (d, *J*=5.93, 2H), 2.60 (t, *J*=8.2 Hz, 2H), 1.45-1.64 (m, 3H) 0.95 (d, *J* = 5.2 Hz, 6H). Spectroscopic data were consistent with literature values.

4-(4-methylpentyl)pyridine (22)[29]

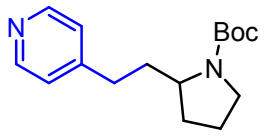


Compound **22** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 2-10 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.3 Hz, 1H), 7.10 (d, *J* = 5.2 Hz, 1H), 2.58 (t, *J* = 7.7 Hz, 2H), 1.69 – 1.49 (m, 4H), 1.36 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 6H). Spectroscopic data were consistent with literature values.

tert-butyl 2-(2-(pyridin-4-yl)ethyl)pyrrolidine-1-carboxylate (23)[33]

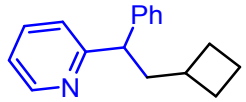


Compound **23** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 4:2:1 (Heptane/DCM/EtOAc) to remove the decomposition products from the catalyst, then 40 % EtOAc/Heptane to get the final pure product.

^{1}H NMR (400 MHz, Chloroform-*d*) (rotamers around the tertiary amide); δ 8.48 (brs, 2H), 7.12 (brs, 2H), 3.86 – 3.77 (m, 1H), 3.41 – 3.31 (m, 2H), 2.62 – 2.60 (m, 2H), 2.0 – 1.95 (m, 1H), 1.91-1.80 (m, 2H), 1.68-1.61 (m, 3H)1.45 (s, 9H). Spectroscopic data were consistent with literature values.

2-(2-cyclobutyl-1-phenylethyl)pyridine (24)[34]



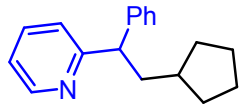
Compound **24** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 5-10 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, J = 4.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.28 (s, 2H), 7.19 (t, J = 7.5 Hz, 2H), 7.08 (t, J = 7.6 Hz, 2H), 7.00 – 6.92 (m, 1H), 4.04 (t, J = 7.8 Hz, 1H), 2.22 – 2.11 (m, 1H), 2.10 – 1.98 (m, 1H), 1.72 – 1.60 (m, 2H), 1.56 – 1.45 (m, 3H), 1.43 – 1.30 (m, 2H), 1.19 (s, 1H), 1.15 – 0.99 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.29, 149.21, 144.10, 136.26, 136.14, 128.40, 128.34, 128.07, 126.26, 122.62, 121.11, 52.87, 41.61, 37.94, 32.86, 32.55, 25.16, 25.14. Spectroscopic data were consistent with literature values.

2-(2-cyclopentyl-1-phenylethyl)pyridine (25)[34]



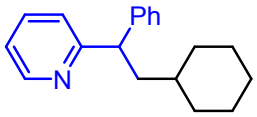
Compound **25** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 5-10 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, J = 4.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.28 (s, 2H), 7.19 (t, J = 7.5 Hz, 2H), 7.08 (t, J = 7.6 Hz, 2H), 7.00 – 6.92 (m, 1H), 4.04 (t, J = 7.8 Hz, 1H), 2.22 – 2.11 (m, 1H), 2.10 – 1.98 (m, 1H), 1.72 – 1.60 (m, 2H), 1.56 – 1.45 (m, 3H), 1.43 – 1.30 (m, 2H), 1.19 (s, 1H), 1.15 – 0.99 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.29, 149.21, 144.10, 136.26, 136.14, 128.40, 128.34, 128.07, 126.26, 122.62, 121.11, 52.87, 41.61, 37.94, 32.86, 32.55, 25.16, 25.14. Spectroscopic data were consistent with literature values.

2-(2-cyclohexyl-1-phenylethyl)pyridine (26)[34]



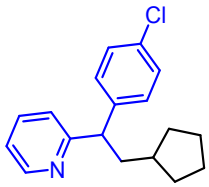
Compound **26** was prepared according to the general procedure (GP1) and isolated as a yellowish oil.

Column Chromatography : Silica, gradient 5-10 % EtOAc/Heptane

^{1}H NMR (400 MHz, Chloroform-d) δ 8.54 (d, J=5.75 Hz, 1H), 7.53 (td, J = 7.7, 1.9 Hz, 1H), 7.34 (d, J = 8.2, Hz, 2H), 7.30-7.24 (m, 2H), 7.17 (d, J= 3.9 Hz, 1H), 7.13 (d, J = 7.5 Hz, 1H), 7.03-7.07 (m, 1H), 4.22 (t, J = 7.9 Hz, 1H), 2.14-2.07 (m, 1H), 2.01-1.94 (m, 1H), 1.80-1.74 (m, 2H), 1.64-1.57 (m, 3H), 1.18-1.05 (m, 4H), 0.97-0.90 (m, 2H).

^{13}C NMR (101 MHz, CDCl3) δ 164.32, 149.20, 144.09, 136.29, 128.40, 128.03, 126.22, 122.58, 121.10, 50.58, 42.74, 35.01, 33.53, 33.19, 26.61, 26.19, 26.15. Spectroscopic data were consistent with literature values.

2-(1-(4-chlorophenyl)-2-cyclopentylethyl)pyridine (27)



Compound **27** was prepared according to the general procedure (GP1) and isolated as a yellow viscous oil.

Column Chromatography : Silica, gradient 0-10 % EtOAc/Heptane

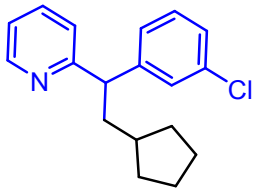
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (ddd, J = 4.9, 1.9, 0.9 Hz, 1H), 7.55 (td, J = 7.7, 1.9 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.26 – 7.22 (m, 2H), 7.14 (dt, J = 7.9, 1.1 Hz, 1H), 7.08 (ddd, J = 7.5, 4.9, 1.2 Hz, 1H), 4.08 (t, J = 7.8 Hz, 1H), 2.21 (dt, J = 13.4, 7.5 Hz, 1H), 2.09 (ddd, J = 13.4, 8.3, 6.7 Hz, 1H), 1.77 – 1.68 (m, 2H), 1.63 – 1.54 (m, 3H), 1.47 – 1.40 (m, 2H), 1.22 – 1.07 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.80, 149.48, 142.67, 136.54, 132.13, 129.53, 128.63, 122.67, 121.46, 52.31, 41.69, 37.96, 32.96, 32.60, 25.25.

IR (neat, ν/cm^{-1}) 2944, 2864, 1587, 1569, 1488, 1470, 1432, 1090, 1014, 822, 746, 545.

HRMS (ESI^+): $[M+H]^+$ cal'd for $C_{18}H_{21}ClN$: 286.1356 found: 286.1350

2-(1-(3-chlorophenyl)-2-cyclopentylethyl)pyridine (28)



Compound **28** was prepared according to the general procedure (GP1) and isolated as a yellow viscous oil.

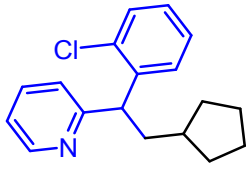
Column Chromatography : Silica, gradient 0-10 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (ddd, J = 4.9, 1.8, 0.8 Hz, 1H), 7.56 (td, J = 7.7, 1.9 Hz, 1H), 7.35-7.33 (m, 1H), 7.25-7.22 (m, 2H), 7.17 – 7.13 (m, 2H), 7.11-7.07 (m, 1H), 4.08 (t, J = 7.9 Hz, 1H), 2.22 (dt, J = 13.5, 7.6 Hz, 1H), 2.12 – 2.03 (m, 1H), 1.78 – 1.67 (m, 2H), 1.62 – 1.55 (m, 3H), 1.43 (m, 2H), 1.20 – 1.10 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.49, 149.51, 146.30, 136.60, 134.28, 129.76, 128.27, 126.60, 126.44, 122.76, 121.55, 52.65, 41.63, 37.95, 32.92, 32.65, 25.26, 25.24.

HRMS (ESI^+): $[M+H]^+$ cal'd for $C_{18}H_{21}ClN$: 286.1356 found: 286.1348

2-(1-(2-chlorophenyl)-2-cyclopentylethyl)pyridine (29)



Compound **29** was prepared according to the general procedure (GP1) and isolated as a yellow viscous oil.

Column Chromatography : Silica, gradient 0-10 % EtOAc/Heptane

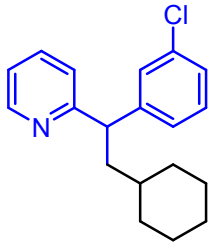
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 – 8.55 (m, 1H), 7.60 – 7.51 (m, 2H), 7.36 (dd, J = 7.9, 1.2 Hz, 1H), 7.30 – 7.20 (m, 2H), 7.24 (dd, J = 10.7, 4.5 Hz, 2H), 7.16 – 7.07 (m, 2H), 4.74 (t, J = 7.7 Hz, 1H), 2.30 (dt, J = 13.5, 7.5 Hz, 1H), 2.14 – 2.05 (m, 1H), 1.80 – 1.74 (m, 2H), 1.68 – 1.57 (m, 3H), 1.51 – 1.42 (m, 2H), 1.24 – 1.15 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.94, 149.52, 141.56, 136.37, 134.11, 129.55, 129.44, 127.49, 127.04, 123.73, 121.45, 47.90, 41.28, 38.12, 32.99, 32.78, 25.30, 25.28.

IR (neat, ν/cm^{-1}) 3063, 3006, 2864, 1586, 1569, 1470, 1431, 1050, 1033, 745, 575.

HRMS (ESI$^+$): $[M+H]^+$ cal'd for $C_{18}H_{21}ClN$: 286.1356, found : 286.1355

2-(1-(3-chlorophenyl)-2-cyclohexylethyl)pyridine (30)



Compound **30** was prepared according to the general procedure (GP1) and isolated as a yellow viscous oil.

Column Chromatography : Silica, gradient 0-10 % EtOAc/Heptane

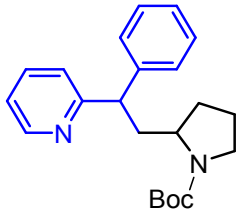
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (tdd, J = 4.8, 1.8, 0.8 Hz, 1H), 7.56 (td, J = 7.7, 1.9 Hz, 1H), 7.33 (t, J = 1.7 Hz, 1H), 7.25 – 7.13 (m, 4H), 7.09 (ddd, J = 7.5, 4.9, 1.0 Hz, 1H), 4.18 (t, J = 7.9 Hz, 1H), 2.19 – 2.01 (m, 1H), 1.92 (ddd, J = 23.4, 15.0, 11.0 Hz, 1H), 1.75 (dd, J = 12.5, 1.5 Hz, 2H), 1.68 – 1.57 (m, 3H), 1.14 – 1.07 (m, 4H), 0.98 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.56, 149.54, 146.37, 136.58, 134.29, 129.77, 128.27, 126.58, 126.43, 122.73, 121.52, 50.45, 42.82, 35.12, 33.56, 33.35, 26.70, 26.29, 26.27.

IR (neat, ν/cm^{-1}) 2920, 2849, 1586, 1569, 1470, 1447, 1429, 9067, 775, 745, 731, 696

HRMS (ESI): $[M+H]^+$ cal'd for found $C_{19}H_{23}ClN$: 300.1513, found: 300.1515

tert-butyl 2-(2-phenyl-2-(pyridin-2-yl)ethyl)pyrrolidine-1-carboxylate (31)



Compound **31** was prepared according to the general procedure (GP1) and isolated as a yellow viscous oil.

Column Chromatography : Silica, gradient 5-10 % EtOAc/Heptane + 2% Et_3N

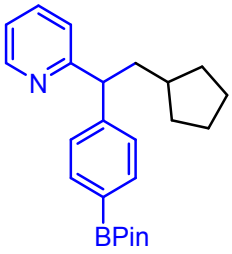
^{1}H NMR (400 MHz, $CDCl_3$, rotameric center) δ 8.52 (d, J = 3.8 Hz, 1H), 7.60 – 7.47 (m, 1H), 7.45 – 7.22 (m, 5H), 7.20 – 7.12 (m, 1H), 7.02 (d, J = 21.4 Hz, 1H), 4.13 (brs, 1H), 3.85 – 3.53 (m, 1H), 3.32 (brs, 2H), 2.94 – 2.43 (m, 1H), 1.98 – 1.89 (m, 1H), 1.87 – 1.61 (m, 4H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.15, 154.51, 149.32, 149.13, 142.45, 136.44, 128.60, 128.52, 128.38, 122.51, 121.37, 79.21, 77.48, 77.16, 76.84, 55.89, 55.66, 51.27, 46.43, 46.02, 39.58, 38.87, 30.45, 30.08, 28.66, 23.81, 23.07, 22.86.

IR (neat, ν/cm^{-1}) 2972, 1679, 1588, 1392, 1364, 1216, 745, 698.

HRMS (ESI^+): $[M+Na]^+$ cal'd for $C_{22}H_{28}N_2O_2Na$: 375.2048 found: 375.2040

2-(2-cyclopentyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethyl)pyridine (32)



Compound **32** was prepared according to the general procedure (GP1) and isolated as a greenish solid. **M.P.**: 127.6 °C

Column Chromatography : Silica, gradient 10-25 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (dd, J = 5.0, 1.6 Hz, 1H), 7.74 (d, J = 7.7 Hz, 2H), 7.52 (td, J = 7.7, 1.8 Hz, 1H), 7.37 (d, J = 7.7 Hz, 2H), 7.14 (d, J = 7.9 Hz, 1H), 7.09 – 7.02 (m, 1H), 4.13 (t, J = 7.9 Hz, 1H), 2.29 – 2.09 (m, 2H), 1.73 (m, 2H), 1.61 – 1.53 (m, 3H), 1.49 – 1.36 (m, 2H), 1.31 (s, 12H), 1.21 – 1.05 (m, 2H).

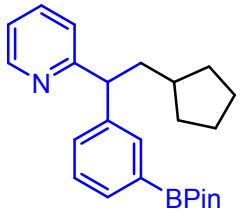
^{13}C NMR (75 MHz, $CDCl_3$) δ 164.08, 149.31, 147.41, 136.44, 135.08, 127.68, 122.76, 121.29, 83.74, 53.13, 41.40, 37.99, 33.01, 32.54, 25.24, 24.96.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.03.

IR (neat, ν/cm^{-1}) 2942, 2861, 1598, 1450, 1356, 1140, 1089, 855, 739.

HRMS (APCI): $[M+2H]^{2+}$ cal'd for $C_{24}H_{34}BNO_2$: 184.1288 found: 184.1131

2-(2-cyclopentyl-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethyl)pyridine (33)



Compound **33** was prepared according to the general procedure (GP1) and isolated as a clear viscous oil.

Column Chromatography : Silica, gradient 10-25 % EtOAc/Heptane

^{1}H NMR (400 MHz, CDCl3) δ 8.55 (dd, J = 4.8, 0.9 Hz, 1H), 7.76 (s, 1H), 7.64 (d, J = 7.3 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.29 (dd, J = 9.0, 6.1 Hz, 1H), 7.16 (t, J = 7.7 Hz, 1H), 7.06 (ddd, J = 7.4, 4.9, 1.0 Hz, 1H), 4.14 (t, J = 7.8 Hz, 1H), 2.28 (dt, J = 13.5, 7.6 Hz, 1H), 2.14 – 2.05 (m, 1H), 1.76 – 1.68 (m, 2H), 1.64 – 1.54 (m, 3H), 1.47 – 1.39 (m, J = 15.0, 4.0 Hz, 2H), 1.33 (s, 12H), 1.19 – 1.12 (m, 2H).

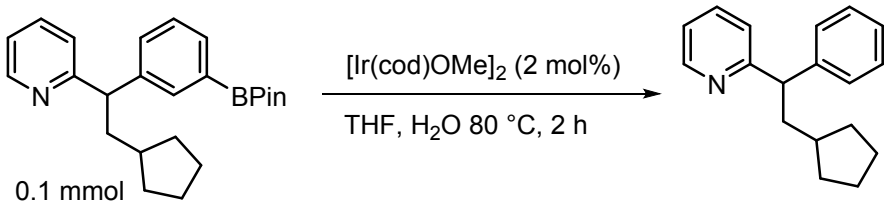
^{13}C NMR (75 MHz, CDCl3) δ 164.08, 149.31, 147.41, 136.44, 135.08, 127.68, 122.76, 121.29, 83.74, 53.13, 41.40, 37.99, 33.01, 32.54, 25.24, 24.96.

^{11}B NMR (128 MHz, CDCl3) δ 31.03.

IR (neat, ν/cm^{-1}) 2941, 2858, 1588, 1355, 1142, 708.

HRMS: We could not observed the exact mass in HRMS in ESI (positive and negative mode) and APCI positive mode.

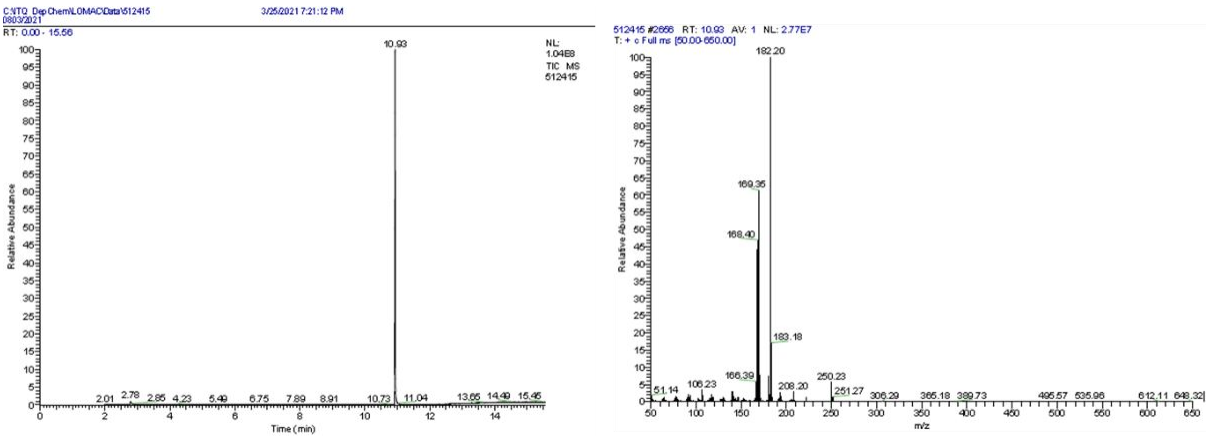
To further confirm the structure we performed protodeboronation following the reported procedure:[13]



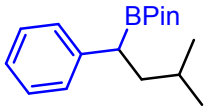
In a flame dried 10 mL reaction vial, compound **33**, $[Ir(cod)OMe]_2$ (2 mol%) and degassed THF (0.3 mL) were added under N_2 followed by addition of water (0.20 mL). The resulting reaction mixture was then placed in a preheated oil bath at 80 °C and stirred for 2 h. Afterwards, the reaction mixture was cooled to room temperature and the crude residue was purified by flash chromatography on silica gel.

Column Chromatography : Silica, gradient 5-10 % EtOAc/Heptane

Spectroscopic data were consistent with compound **25**.



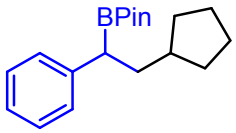
4,4,5,5-tetramethyl-2-(3-methyl-1-phenylbutyl)-1,3,2-dioxaborolane (34)[35,36]



Compound **34** was prepared according to the general procedure (GP1) and yield was determined by ^{1}HNMR using dibromomethane as an internal standard.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.24 (m, 4H), 7.18-7.13 (m, 1H), 2.46 (t, J = 8.0 Hz, 1H), 1.71 (qd, J = 13.3, 6.5 Hz, 2H), 1.51 (dt, J = 19.4, 6.2 Hz, 1H), 1.23 (s,6), 1.22 (s, 6H), 0.93 (t, J = 6.2 Hz, 6H). Spectroscopic data were consistent with literature values.

2-(2-cyclopentyl-1-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (35)



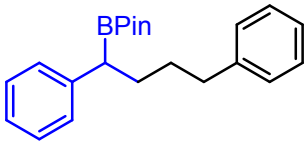
Compound **35** was prepared according to the general procedure (GP1) and yield was determined by ^{1}HNMR using dibromomethane as an internal standard.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.24 (m, 4H), 7.18-7.13 (m,1H), 2.41 (t, J = 7.7 Hz, 1H), 1.85 – 1.70 (m, 4H), 1.64 – 1.44 (m, 7H), 1.23 (d, J = 4.4 Hz, 12H).

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.89.

Note: Characteristic peak appeared at 2.34 (t, j = 7.39, 1H).

2-(1,3-diphenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (36)[36]



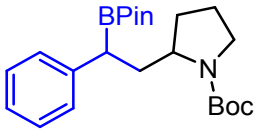
Compound **36** was prepared according to the general procedure (GP1) and isolated as white solid.

Column Chromatography : Silica, gradient 5-10 % Et_2O/*iso*-Hexane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 6H), 7.25 – 7.17 (m, 4H), 2.74 – 2.64 (m, 2H), 2.42 (t, J = 7.7 Hz, 1H), 2.00 (tt, J = 15.4, 7.9 Hz, 1H), 1.81 (dt, J = 20.6, 7.4 Hz, 1H), 1.73 – 1.62 (m, 2H), 1.28 (s, 6H), 1.26 (s, 6H).

^{11}B NMR (128 MHz, $CDCl_3$) δ 33.97. Spectroscopic data were consistent with literature values.

tert-butyl 2-(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)pyrrolidine-1-carboxylate (37)



Compound **37** was prepared according to the general procedure (GP1) and isolated as a yellow viscous oil.

Column Chromatography : Silica, gradient 5-20 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$ rotameric center) δ 7.16 (m, 5H), 3.81 (brs, 1H), 3.31 (brs, 2H), 2.36 (m, 2H), 1.99 – 1.63 (m, 5H), 1.49 (s, 9H), 1.17 (d, J = 5.2 Hz, 12H).

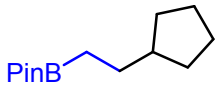
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.81, 143.41, 128.43, 128.39, 125.34, 83.43, 79.17, 57.98, 46.04, 37.65, 30.91, 28.78, 28.72, 24.76, 24.66, 23.22.

^{11}B NMR (128 MHz, $CDCl_3$) δ 32.70.

IR (neat, ν/cm^{-1}) 3363, 2975, 1667, 1474, 1391, 1147, 850, 731, 698.

HRMS (ESI^+): $[M+2Na]^{2+}$ cal'd for $C_{23}H_{36}BNNa_2O_4$: 218,121418 found: 218.1175.

2-(2-cyclopentylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (38)[37]



Compound **38** was prepared according to the general procedure (GP1) and isolated as a yellow viscous oil.

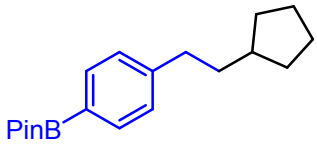
Column Chromatography : Silica, gradient 2-5 % Et_2O/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.71-1.67 (m, 3H), 1.62 – 1.36 (m, 6H), 1.24 (s, 12H), 1.06-1.02 (m, 4H), 0.82 – 0.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 82.92, 42.78, 32.48, 30.30, 25.36, 24.87.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.73. Spectroscopic data were consistent with literature values.

2-(4-(2-cyclopentylethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (39)



Compound **39** was prepared according to the general procedure (GP1) and isolated as a white solid.

M.P.: 55 °C

Column Chromatography : Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 2.67 – 2.60 (m, 2H), 1.83 – 1.72 (m, 3H), 1.62 (ddd, J = 8.2, 7.7, 4.9 Hz, 4H), 1.56 – 1.45 (m, 2H), 1.35 (s, 12H), 1.18 – 1.05 (m, 2H).

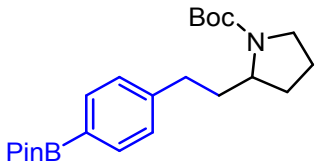
^{13}C NMR (75 MHz, $CDCl_3$) δ 146.69, 134.95, 127.99, 83.73, 39.78, 38.08, 35.50, 32.78, 25.37, 25.00.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.27.

IR (neat, ν/cm^{-1}) 2949, 2862, 1611, 1357, 1318, 1143, 1088, 859, 656

HRMS (APCI): $[M+H]^+$ cal'd for $C_{19}H_{30}BO_2$: 410.2240 found: 410.6688

tert-butyl 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenethyl)pyrrolidine-1-carboxylate (40)



Compound **40** was prepared according to the general procedure (GP1) and isolated as a yellow solid. **M.P.**: 101.8 °C

Column Chromatography : Silica, gradient 2-15 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$, rotameric center) δ 7.72 (d, J = 7.4 Hz, 2H), 7.20 (d, J = 7.3 Hz, 2H), 3.80 (brs, J = 28.0 Hz, 1H), 3.36 (brs, 2H), 2.61 (d, J = 7.9 Hz, 2H), 2.00 – 1.87 (m, 1H), 1.86 – 1.74 (m, 2H), 1.71 – 1.57 (m, 3H), 1.45 (s, 9H), 1.33 (s, 12H).

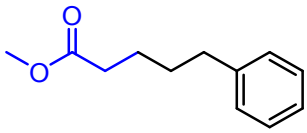
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.75, 145.56, 135.04, 127.91, 83.75, 79.21, 77.48, 77.16, 76.84, 57.39, 57.07, 53.54, 46.61, 46.29, 36.30, 35.99, 33.13, 30.76, 30.26, 28.68, 24.97.

^{11}B NMR (128 MHz, $CDCl_3$) δ 32.21.

IR (neat, ν/cm^{-1}) 2975, 2930, 1667, 1515, 1474, 1366, 981, 850, 698, 672.

HRMS (ESI^+): $[M+CH_3OH+H]^+$ cal'd for $C_{24}H_{41}BNO_5$: 423.2978 found: 423.2661

methyl 5-phenylpentanoate(41)[38]



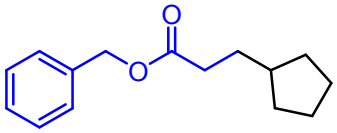
Compound **41** was prepared according to the general procedure (GP1) and isolated as a clear oil.

Column Chromatography : Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 – 7.14 (m, 2H), 7.11-7.07 (m, 3H), 3.57 (s, 3H), 2.55 (t, J = 6.3 Hz, 2H), 2.29 – 2.19 (m, 2H), 1.59 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.14, 142.22, 128.48, 128.42, 125.88, 51.57, 35.68, 34.05, 31.00, 24.70. Spectroscopic data were consistent with literature values.

benzyl 3-cyclopentylpropanoate (42)[39]



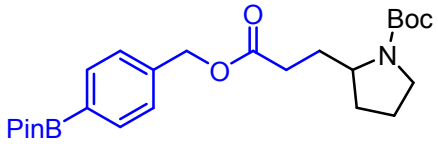
Compound **42** was prepared according to the general procedure (GP1) and isolated as a clear oil.

Column Chromatography : Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 5H), 5.12 (s, 2H), 2.41 – 2.34 (m, 2H), 1.75 (m, 3H), 1.71 – 1.64 (m, 2H), 1.60 (m, 2H), 1.51 (m, 2H), 1.16 – 1.02 (m, 2H).

Spectroscopic data were consistent with literature values.

tert-butyl 2-(3-oxo-3-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)oxy)propyl)pyrrolidine-1-carboxylate (43)



Compound **43** was prepared according to the general procedure (GP1) and isolated as a clear oil.

Column Chromatography : Silica, gradient 5-20 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 5.12 (s, 2H), 3.78 (brs, 1H), 3.46 – 3.20 (m, 2H), 2.36 (m, 2H), 2.03 – 1.56 (m, 6H), 1.45 (s, 9H), 1.34 (s, 12H).

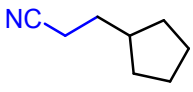
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.28, 154.88, 139.18, 135.12, 127.40, 83.98, 79.44, 66.21, 56.73, 46.53, **46.35**, 31.46, 30.99, **30.82**, 29.83, 28.67, 25.00, 23.19.

^{11}B NMR (128 MHz, CDCl3) δ 31.22.

IR (neat, ν/cm^{-1}) 2975, 1736, 1689, 1391, 1358, 1142, 1087, 858, 730, 656.

HRMS (ESI^+): $[M+CH_3OH+H]^+$ cal'd for $C_{26}H_{43}BNO_7$: 481.3105 found: 482.2681

3-cyclopentylpropanenitrile (44)[40]

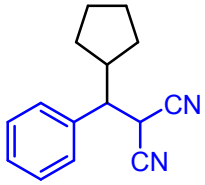


Compound **44** was prepared according to the general procedure (GP1) and isolated as a clear oil.

Column Chromatography : Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, CDCl3) δ 2.26-2.21 (m, 2H), 1.71 – 1.61 (m, 3H), 1.60 – 1.38 (m, 6H), 1.0-0.93 (m, 2H). Spectroscopic data were consistent with literature values.

2-(cyclopentyl(phenyl)methyl)malononitrile (45)[41]

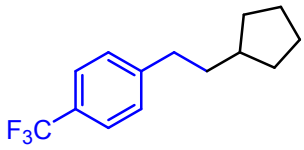


Compound **45** was prepared according to the general procedure (GP1) and isolated as a clear oil.

Column Chromatography : Silica, gradient 5-15 % EtOAc/Heptane

^{1}H NMR (400 MHz, CDCl3) δ 7.45 – 7.33 (m, 5H), 4.10 (d, J = 4.6 Hz, 1H), 2.93 (dd, J = 11.0, 4.6 Hz, 1H), 2.62 – 2.47 (m, 1H), 2.05 (dtd, J = 11.1, 7.3, 3.7 Hz, 1H), 1.82 – 1.54 (m, 4H), 1.35 – 1.24 (m, 1H), 1.10 – 1.01 (m, 1H). Spectroscopic data were consistent with literature values.

1-(2-cyclopentylethyl)-4-(trifluoromethyl)benzene (46)



Compound **46** was prepared according to the general procedure (GP1) and isolated as a clear oil.

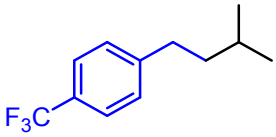
Column Chromatography : Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, CDCl3) δ 7.54 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 2.72 – 2.64 (m, 2H), 1.86 – 1.76 (m, 3H), 1.69 – 1.61 (m, 4H), 1.59 – 1.50 (m, 2H), 1.21 – 1.08 (m, 2H). **^{13}C NMR** (101 MHz, CDCl3) δ 147.33 (d, J = 1.2 Hz), 128.78, 128.12 (q, J = 32.2 Hz), 125.9 (q, J = 270 Hz), 125.3 (q, J = 3.8 Hz), 39.75, 37.97, 35.16, 32.78, 25.38.

IR (neat, ν/cm^{-1}) 2944, 2860, 2862, 1324, 1122, 1066, 1018.

HRMS (APCI): $[M+H]^+$cal'd for $C_{14}H_{18}F_3$: 243.1355 found: 243.1133

1-isopentyl-4-(trifluoromethyl)benzene (47)[42]

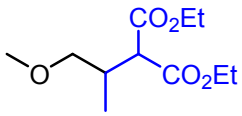


Compound **47** was prepared according to the general procedure (GP1) and isolated as a clear oil.

Column Chromatography : Silica, gradient 2-8 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 2.69 – 2.64 (m, 2H), 1.59 (m, 1H), 1.51 (m, 2H), 0.94 (d, J = 6.4 Hz, 6H). Spectroscopic data were consistent with literature values.

diethyl 2-(1-methoxypropan-2-yl)malonate (48)[43]

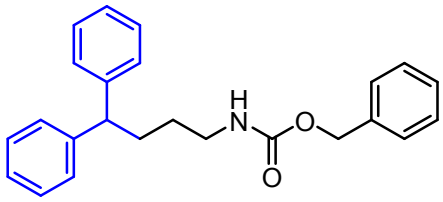


Compound **48** (48 % yield) was prepared according to the general procedure in flow (GP1) and isolated as a clear oil.

Column Chromatography : Silica, gradient 4-12 % EtOAc/Heptane (TLC stain: $KMnO_4$)

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.24 – 4.13 (m, 4H), 3.42 (d, J = 7.5 Hz, 1H), 3.33 (d, J = 5.9 Hz, 1H), 3.30 (s, 1H), 2.53 (m, 1H), 1.26 (m, 6H), 1.02 (d, J = 6.9 Hz, 1H). Spectroscopic data were consistent with literature values.

benzyl (4,4-diphenylbutyl)carbamate (49)



Compound **49** was prepared according to the general procedure in flow (GP1) and isolated as a yellow oil.

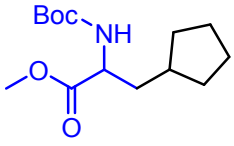
Column Chromatography : Silica, gradient 5-25 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 15H), 5.14 (s, 2H), 4.87 (s, 1H), 3.95 (t, J = 7.7 Hz, 2H), 3.25 (dd, J = 13.0, 6.6 Hz, 2H), 2.12 (dd, J = 15.5, 7.8 Hz, 2H), 1.51 (dt, J = 14.5, 7.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.42, 144.74, 136.70, 128.52, 128.11, 128.09, 127.82, 126.25, 77.48, 77.16, 76.84, 66.57, 51.01, 40.95, 32.71, 28.55.

GS-MS (EI^+): 360.3

methyl 2-((tert-butoxycarbonyl)amino)-3-cyclopentylpropanoate (50)[44]

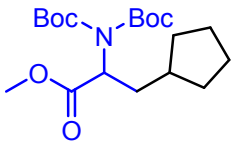


Compound **50** was prepared according to the general procedure (GP1) and isolated as a clear oil.

Column Chromatography : Silica, gradient 2-20 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.98 (d, J = 7.5 Hz, 2H), 4.37 – 4.25 (m, 2H), 3.75 (s, 3H), 1.91 – 1.75 (m, 4H), 1.71 – 1.60 (m, 5H), 1.18 – 1.09 (m, 2H). Spectroscopic data were consistent with literature values.

methyl 2-(Bis(tert-butoxycarbonyl)amino)-3-cyclopentylpropanoate (51)



Compound **51** was prepared according to the general procedure (GP1) and isolated as a clear oil.

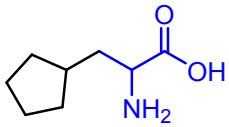
Column Chromatography : Silica, gradient 2-10 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (dd, J = 9.6, 5.0 Hz, 1H), 3.70 (s, 3H), 2.05 (m, 1H), 1.99 – 1.89 (m, 1H), 1.86 – 1.70 (m, 3H), 1.66 – 1.55 (m, 4H), 1.49 (s, 18H) 1.18 – 1.05 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.86, 152.24, 83.07, 57.84, 52.24, 37.07, 36.13, 33.04, 32.59, 28.12, 25.30, 25.14.

IR (neat, ν/cm^{-1}) 2980, 2952, 1788, 1740, 1698, 1477, 1455, 1367, 1134, 908, 728.

HRMS (ESI$^+$): $[M+Na]^+$ cal'd for $C_{19}H_{33}NNaO_6$: 394.2204 found: 394.2200.

2-amino-3-cyclopentylpropanoic acid[45]

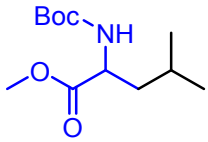


Compound **51** (0.2 mmol) was dissolved in aqueous 6 M HCl (2 mL) and heated to 125 °C for 24 h. After complete hydrolysis, solvent was removed *in vacuo* at 60 °C. The crude solid was re-dissolved in water and washed with Et_2O. Removal of solvent *in vacuo* afforded the amino acid hydrochloride as white crystals.[1]

^{1}H NMR (400 MHz, D_2O) δ 4.00 (t, J = 6.4 Hz, 1H), 2.04 – 1.90 (m, 3H), 1.88 – 1.79 (m, 2H), 1.69 – 1.61 (m, 2H), 1.55 (m, 1H), 1.17 (m, 2H).

^{13}C NMR (101 MHz, D_2O) δ 175.64, 55.41, 38.72, 37.99, 34.54, 34.21, 27.12, 26.91.

methyl (tert-butoxycarbonyl)leucinate (52)[44]

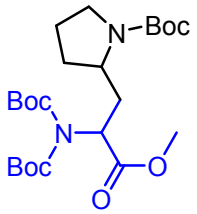


Compound **52** was prepared according to the general procedure (GP1) and isolated as a clear oil.

Column Chromatography : Silica, gradient 2-20 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.93 (d, J = 7.6 Hz, 1H), 4.30 (dd, J = 13.8, 8.6 Hz, 1H), 3.71 (s, 3H), 1.67 (dd, J = 13.1, 6.5 Hz, 1H), 1.62 – 1.53 (m, 1H), 1.53 – 1.47 (m, 1H), 1.42 (s, 9H), 0.92 (dd, J = 6.5, 2.6 Hz, 6H). Spectroscopic data were consistent with literature values.

tert-Butyl 3-(2-((Bis(*tert*-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)pyrrolidine-1-carboxylate (53)



Compound **53** was prepared according to the general procedure (GP1) using $[Ir\{dF(CF_3)ppy\}_2(dtbpy)]PF_6$ (3 mol%) and isolated as a yellow solid. **M.P.**: 96.3 °C

Column Chromatography : Silica, gradient 2-22 % EtOAc/Heptane

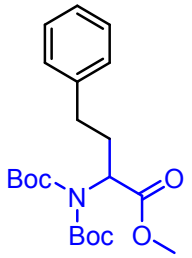
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 – 4.70 (m, 1H), 3.82 (brs, 1H), 3.64 (s, 3H), 3.38 – 3.15 (m, 2H), 1.78 (m, 6H), 1.46 – 1.28 (m, 27H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.97, 154.40, 151.94, 83.07, 79.27, 56.70, **56.06**, 52.19, 45.99, 36.05, **35.48**, 31.03, **30.59**, 28.51, 27.98, 23.82, **23.14**.

IR (neat, ν/cm^{-1}) 2973, 1736, 1687, 1392, 1163, 1143.

HRMS (ESI^+): $[M+Na]^+$ cal'd for $C_{23}H_{40}N_2NaO_8$: 495.2681 found: 498.2679.

Methyl 2-(Bis(tert-butoxycarbonyl)amino)-4-phenylbutanoate(54)[46]



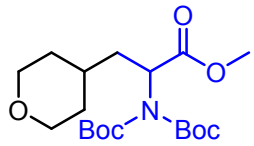
Compound **54** was prepared according to the general procedure (GP1) and isolated as a liquid.

Column Chromatography : Silica, gradient 5-20 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.18 (m, 3H), 4.91 (dd, J = 9.4, 5.3 Hz, 1H), 3.71 (s, 3H), 2.71 – 2.65 (m, 2H), 2.46 (m, 1H), 2.26 – 2.14 (m, 1H), 1.49 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.35, 152.19, 141.32, 128.52, 128.48, 126.11, 83.22, 57.86, 52.26, 32.64, 31.83, 28.08. Spectroscopic data were consistent with literature values.

tert-Butyl 3-(2-((Bis(*tert*-butoxycarbonyl)amino)-3-methoxy-3- (tetrahydro-2H-pyran-4-yl)-1-carboxylate (55)



Compound **55** was prepared according to the general procedure (GP1) and isolated as a liquid.

Column Chromatography : Silica, gradient 5-15 % EtOAc/Heptane

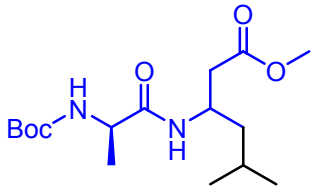
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.95 (dd, J = 9.3, 5.0 Hz, 1H), 3.97 – 3.88 (m, 2H), 3.70 (s, 3H), 3.33 (q, J = 11.5 Hz, 2H), 2.08 – 1.93 (m, 2H), 1.90 – 1.78 (m, 1H), 1.72 (d, J = 13.5 Hz, 2H), 1.49 (s, 18H), 1.23 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.64, 152.25, 83.29, 68.08, 67.99, 55.53, 52.34, 37.31, 33.54, 32.74, 32.12, 28.10.

IR (neat, ν/cm^{-1}) 2978, 2931, 2841, 1793, 1744, 1698, 1365, 1248, 1125, 857, 731.

HRMS (ESI^+): $[M+Na]^+$ cal'd for $C_{19}H_{33}NNaO_7$: 410.2153 found: 410.2148.

Methyl 3-(2-((tert-butoxycarbonyl)amino)propanamido)-5-methylhexanoate(56)[47]



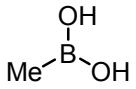
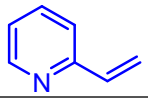
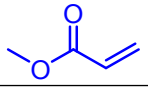
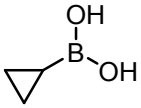
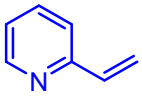
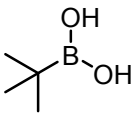
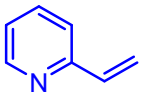
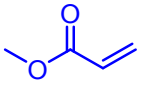
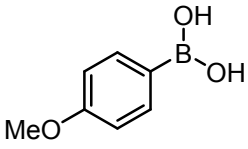
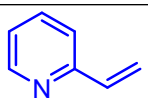
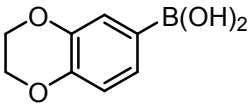
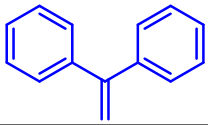
Compound **56** was prepared according to the general procedure in flow (GP1) and isolated as a white solid.

Column Chromatography : Silica, gradient 5-40 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.60 (s, 1H), 4.99 (s, 1H), 4.64 – 4.55 (m, 1H), 4.16 (br s, 1H), 3.72 (s, 3H), 1.67-1.60 (m, 2H), 1.57-1.51 (m, 1H), 1.44 (s, 9H), 1.35 (dd, J = 6.9, 2.6 Hz, 3H), 0.91 (br s, 6H). Spectroscopic data were consistent with literature values.

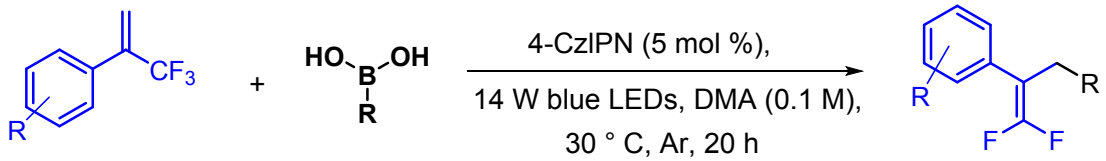
Note: We observed the severe decomposition of the photocatalyst which interfered in the isolation of the product.

Table S7: Unsuccessful substrates[a]

Entry	Boronic Acid	Alkene Acceptor	Yield (%)[b]
1			0
2			0
3			0
4			0
5			10
6			10 The major side product was anisole, whose formation could be due to HAT between solvent and aryl radical.
7			20

[a]Reaction conditions: 1 equiv (0.22 mmol) of **BA**, 1.5 equiv of **alkene**, 5 mol % of the photocatalyst. [b] Yields were determined by ^{1}H-NMR using 3,4,5-trimethoxybenzaldehyde as internal standard.

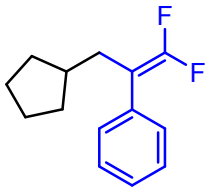
1.6. General procedure for the defluorinative alkylation of -CF_3 containing alkenes/ allylation reaction (GP2)



An oven-dried 10 mL glass vial equipped with a magnetic stirring bar was charged with alkyl boronic acid (1.5 equiv, 0.66 mmol), photoredox catalyst (4CzIPN, 5 mol%) and DMA (0.1 M). The vial was closed with a silicon septum and purged with argon three times. The vial was then charged with -CF_3 containing alkene (1 equiv, 0.44 mmol) and irradiated with a commercial blue LED strip (14 W, 450 nm) for 20 hours in the aforementioned photoreactor. The progress of the reaction was monitored by TLC and GC/MS. After completion, the solution was diluted with Et_2O and transferred in a separatory funnel containing deionized water. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4. Purification was performed by SiO_2 column chromatography.

***Note**: Water bath temperature of the rotavapor was set at 35°C.

(3-cyclopentyl-1,1-difluoroprop-1-en-2-yl)benzene (57)[48]

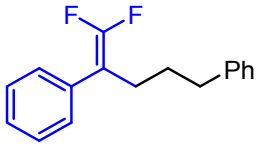


Compound **57** was prepared according to the general procedure (GP2) and isolated as a clear oil.

Column Chromatography : Silica, Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.21 (m, 5H), 2.40 – 2.37 (m, 2H), 1.78 (dq, J = 14.7, 7.3 Hz, 1H), 1.71 – 1.55 (m, 4H), 1.50 – 1.40 (m, 2H), 1.19 – 1.03 (m, 2H). Spectroscopic data were consistent with literature values.

(5,5-difluoropent-4-ene-1,4-diyl)dibenzene (58)



Compound **58** was prepared according to the general procedure (GP2) and isolated as oil.

Column Chromatography : Silica, gradient 0-1 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (dd, J = 8.2, 6.6 Hz, 2H), 7.28 – 7.20 (m, 5H), 7.18 – 7.13 (m, 1H), 7.13 – 7.06 (m, 2H), 2.65 – 2.53 (m, 2H), 2.42 (tt, J = 7.5, 2.4 Hz, 2H), 1.68 (p, J = 7.7 Hz, 2H).

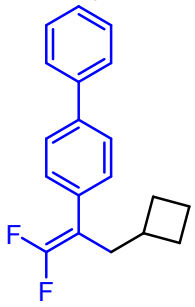
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.72 (dd, J = 289.2, 287.6 Hz), 141.97 , 133.73 (d, J = 2.4 Hz), 128.56 , 128.48 , 128.43 , 128.39 , 127.38 , 125.95 , 92.31 (dd, J = 19.2, 15.5 Hz), 35.36 , 29.53 (t, J = 2.5 Hz), 27.42 .

^{19}F NMR (377 MHz, $CDCl_3$) δ -91.52 (d, J = 44.0 Hz), -91.65 (d, J = 44.0 Hz).

IR (neat, ν/cm^{-1}) 3061, 2932, 2862, 1726, 1496, 1446, 1229, 1118, 719, 694, 492.

HRMS (APCI): $[M+H]^+$ cal'd for $C_{17}H_{17}F_2$: 259.1293 found: 259.1278

4-(3-cyclobutyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl(59)[49]

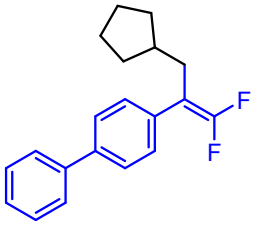


Compound **59** was prepared according to the general procedure (GP2) and isolated as white solid.

Column Chromatography : Silica, gradient 0-4 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 4H), 7.48 – 7.42 (m, 2H), 7.38 – 7.33 (m, 3H), 2.52 (dt, J = 7.6, 2.3 Hz, 2H), 2.42 – 2.28 (m, 1H), 2.02 – 1.94 (m, 2H), 1.84 – 1.76 (m, 2H), 1.72 – 1.62 (m, 2H). Spectroscopic data were consistent with literature values.

1-(3-cyclopentyl-1,1-difluoroprop-1-en-2-yl)-4-(phenylethynyl)benzene (60)



Compound **60** was prepared according to the general procedure (GP2) and isolated as white solid.

M.P.: 45.7 °C

Column Chromatography : Silica, gradient 0-4 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 11.4, 4.0 Hz, 4H), 7.51 – 7.35 (m, 6H), 2.47 (dd, J = 5.5, 2.0 Hz, 2H), 1.94 – 1.84 (m, 1H), 1.77 – 1.68 (m, 4H), 1.53-1.51 (m, 2H), 1.25 – 1.15 (m, 2H).

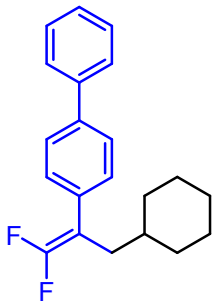
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.11 (dd, J = 290.0, 286.2 Hz), 140.76, 140.08, 133.13 (dd, J = 3.0, 4.4 Hz), 128.93, 128.85 (dd, J = 3.7, 3.2 Hz), 127.49, 127.18, 127.15, 92.19 (dd, J = 22.0, 12.6 Hz), 38.44 (t, J = 2.3 Hz), 33.62, 32.31, 25.14. (dd peak at 128.85 partially overlaps with 128.93 peak)

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.55 (d, J = 44.5 Hz), -91.96 (d, J = 44.5 Hz).

IR (neat, ν/cm^{-1}) 2948, 1728, 1486, 1228, 1107, 1143, 799, 729.

HRMS (ESI^+): $[M+H]^+$ cal'd for $C_{20}H_{21}F_2$: 299.1605 found: 299.1598

4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)-1,1'-biphenyl (61)[35]



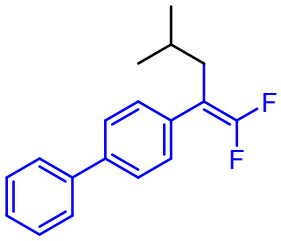
Compound **61** was prepared according to the general procedure (GP2) and isolated as white solid.

Column Chromatography : Silica, gradient 0-4 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 4H), 7.54 – 7.33 (m, 5H), 2.37 (dt, J = 7.1, 2.3 Hz, 2H), 1.78-1.66 (m, J = 20.6, 7.9 Hz, 5H), 1.43 – 1.28 (m, 1H), 1.20-1.18 (m, J = 5.6 Hz, 3H), 1.04-0.93 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -90.63 (d, J = 43.3 Hz), -91.18 (d, J = 43.2 Hz). Spectroscopic data were consistent with literature values.

1-(1,1-difluoro-4-methylpent-1-en-2-yl)-4-(phenylethynyl)benzene (62)



Compound **62** was prepared according to the general procedure (GP2) and isolated as white solid.

Column Chromatography : Silica, gradient 0-4 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 4H), 7.47-7.37 (m, 5H), 2.31 (ddd, J = 7.3, 4.8, 2.6 Hz, 2H), 1.64 (td, J = 13.6, 6.8 Hz, 1H), 0.92 (d, J = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.27 (dd, J = 290.4, 286.4 Hz), 140.75, 140.08, 133.10 (dd, J = 4.4, 3.3 Hz), 128.93, 128.78 (t, J = 3.3 Hz), 127.50, 127.21, 127.16, 91.52 (dd, J = 22.0, 12.6 Hz), 36.67 (d, J = 0.9 Hz), 26.62 (t, J = 2.4 Hz), 22.24.

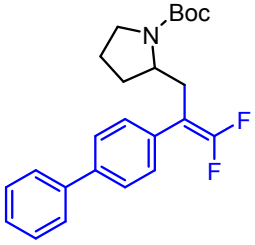
^{19}F NMR (376 MHz, $CDCl_3$) δ -91.01 (d, J = 43.5 Hz), -91.51 (d, J = 43.4 Hz).

IR (neat, ν/cm^{-1}) 2953, 2870, 1912, 1522, 1486, 1460, 1222, 1135, 770, 759, 728, 693, 625, 599.

HRMS (ESI^+): $[M+H]^+$ cal'd for $C_{19}H_{19}F_2$: 273.1449 found: 272.1454

HRMS (APCI): [M] cal'd for $C_{18}H_{18}F_2$: 272.1376 found: 272.1358

tert-butyl 2-(3,3-difluoro-2-(4-(phenylethynyl)phenyl)allyl)pyrrolidine-1-carboxylate (63)



Compound **63** was prepared according to the general procedure (GP2) and isolated as viscous oil.

Column Chromatography : Silica, gradient 5-10 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$, rotameric center) δ 7.49 (m, 9H), 3.93 (s, 1H), 3.40 (s, 2H), 2.95 – 2.91 (d, J = 11.61, 1H), 2.56 – 2.33 (m, 1H), 1.96 – 1.64 (m, 4H), 1.50 (brs, 9H).

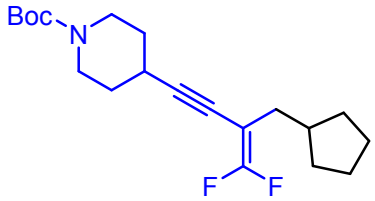
^{13}C NMR (75 MHz, $CDCl_3$) δ 154.50, 140.56, 140.31, 132, 128.89, 128.59 (t, J = 3.5 Hz), 127.55, 127.23, 127.08, 90.03 (dd, J = 26.0, 9.6 Hz), 55.61 (t, J = 3.0 Hz), 46.78, 46.37, 31.98, 31.57, 29.58, 29.12, 29.67, 22.78, 22.74 (CF_2 peak could not be observed due to the presence of rotameric carbon center).

^{19}F NMR (376 MHz, $CDCl_3$) δ -89.36 (d, J = 39.9 Hz), -89.53 (d, J = 40.1 Hz), -89.78 (s).

IR (neat, ν/cm^{-1}) 2973, 1686, 1391, 1285, 1160, 1105, 762, 729, 696.

HRMS (ESI$^+$): $[M+Na]^+$ cal'd for $C_{24}H_{27}F_2NNaO_2$: 422.1906 found: 422.1896.

tert-butyl 4-(3-(cyclopentylmethyl)-4,4-difluorobut-3-en-1-yn-1-yl)piperidine-1-carboxylate (64)



Compound **64** was prepared according to the general procedure (GP2) and isolated as a clear viscous oil.

Column Chromatography : Silica, gradient 0-5 % EtOAc/Heptane ($KMnO_4$ stain)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.64 (ddd, J = 12.9, 6.9, 3.5 Hz, 2H), 3.24 (ddd, J = 13.4, 8.1, 3.5 Hz, 2H), 2.72 (tt, J = 7.8, 3.9 Hz, 1H), 2.02 (s, 2H), 1.82 – 1.72 (m, 4H), 1.66 – 1.56 (m, 4H), 1.55 – 1.50 (m, 2H), 1.45 (s, 9H), 1.25 (s, 1H), 1.14 (dt, J = 13.9, 7.0 Hz, 2H).

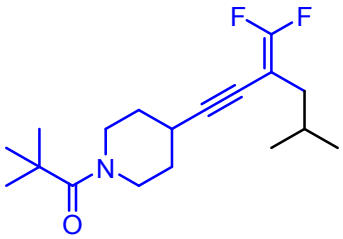
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.28 (dd, J = 294.0, 291.0 Hz), 154.90, 95.77 (t, J = 5.7 Hz), 79.61, 78.15 (dd, J = 34.3, 14.5 Hz), 74.23 (dd, J = 8.1, 3.7 Hz), 66.99, 42.12 (br s), 38.79 (t, J = 2.2 Hz), 33.29 (d, J = 1.5 Hz), 32.22, 31.46, 28.59, 27.72, 25.15, 22.83.

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.45 (d, J = 22.7 Hz), -87.07 (d, J = 22.8 Hz).

IR (neat, ν/cm^{-1}) 2926, 2865, 1693, 1425, 1366, 1161.

HRMS (ESI$^+$): $[M+K]^+$ cal'd for $C_{20}H_{29}F_2NOK$: 376.1848 found: 376.2063

1-(4-(3-(difluoromethylene)-5-methylhex-1-yn-1-yl)piperidin-1-yl)-2,2-dimethylpropan-1-one (65)



Compound **65** was prepared according to the general procedure (GP2) and isolated as a clear viscous oil.

Column Chromatography : Silica, gradient 0-5 % EtOAc/Heptane ($KMnO_4$ stain)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (ddd, J = 13.2, 7.0, 3.5 Hz, 2H), 3.25 (ddd, J = 13.5, 8.0, 3.6 Hz, 2H), 2.71 (dp, J = 7.7, 4.0 Hz, 1H), 1.91 – 1.86 (m, 2H), 1.88 – 1.71 (m, 3H), 1.63 – 1.53 (m, 2H), 1.47 – 1.41 (m, 9H), 0.91 (d, J = 6.4 Hz, 6H).

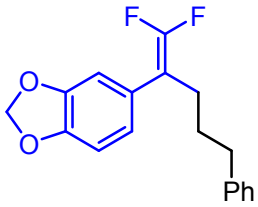
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.40 (dd, J = 294.2, 291.2 Hz), 154.88 , 95.77 (t, J = 5.7 Hz), 79.60 , **77.78-77.29**, 74.13 (dd, J = 8.1, 3.7 Hz), 42.29 , 37.17 (d, J = 2.4 Hz), 36.37 (d, J = 1.3 Hz), 31.45 , 28.57 , 27.67 , 27.13 (t, J = 2.3 Hz), 22.09 (peak of alkyne carbon partially overlaps with $CDCl_3$ peak).

^{19}F NMR (376 MHz, $CDCl_3$) δ -82.12 (d, J = 21.5 Hz), -86.88 (d, J = 21.1 Hz).

IR (neat, ν/cm^{-1}) 2957, 2870, 1692, 1365, 1232, 1164, 1087, 860, 731.

HRMS (ESI^+): $[M+K]^+$ cal'd for $C_{18}H_{27}F_2NOK$: 350.1691 found: 350.1909.

5-(1,1-difluoro-5-phenylpent-1-en-2-yl)benzo[d][1,3]dioxole (66)



Compound **66** was prepared according to the general procedure (GP2) and isolated as oil.

Column Chromatography : Silica, gradient 0-2 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.22 (m, 2H), 7.18 – 7.15 (m, 1H), 7.12 – 7.09 (m, 2H), 6.79 – 6.70 (m, 3H), 5.93 (s, 2H) 2.61 – 2.55 (m, 2H), 2.36 (tt, J = 7.6, 2.4 Hz, 2H), 1.72 – 1.62 (m, 2H).

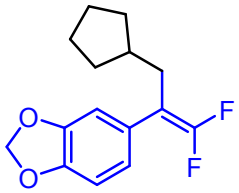
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.63 (dd, J = 289.1, 286.3 Hz), 147.84 , 146.84 , 141.95 , 128.45 (d, J = 3.5 Hz), 127.33 (dd, J = 4.3, 2.9 Hz), 125.96 , 121.92 (t, J = 3.1 Hz), 108.92 (t, J = 3.3 Hz), 108.41 , 101.23 , 92.06 (dd, J = 22.2, 13.4 Hz), 29.43 (t).

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.80 (d, J = 45.1 Hz), -92.14 (d, J = 45.1 Hz).

IR (neat, ν/cm^{-1}) 3026, 1727, 1503, 1489, 1237, 1038, 961, 935, 810, 697, 558.

HRMS (ESI^+): $[M+H]^+$ cal'd for $C_{18}H_{17}F_2O_2$: 303.1191 found: 303.1092.

5-(3-cyclopentyl-1,1-difluoroprop-1-en-2-yl)benzo[d][1,3]dioxole (67)



Compound **67** was prepared according to the general procedure (GP2) and isolated as oil.

Column Chromatography : Silica, gradient 0-2 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85 – 6.70 (m, 3H), 5.96 (s, 2H), 2.33 (dt, J = 7.6, 2.5 Hz, 2H), 1.81 (dt, J = 14.9, 7.4 Hz, 1H), 1.75 – 1.55 (m, 4H), 1.54 – 1.40 (m, 2H), 1.14 (td, J = 14.1, 6.9 Hz, 2H).

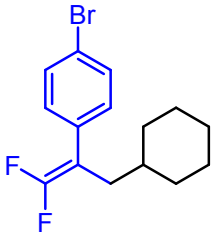
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.94 (dd, J = 287.9, 286.3 Hz), 147.75 , 146.76 , 127.81 (d, J = 2.3 Hz), 122.01 (t, J = 3.1 Hz), 109.06 (t, J = 3.2 Hz), 108.36 , 101.22 , 92.21 (dd, J = 20.2, 15.3 Hz), 38.28 (t, J = 2.4 Hz), 34.03 , 32.25 , 25.12.

^{19}F NMR (377 MHz, $CDCl_3$) δ -92.66 (d, J = 46.8 Hz), -92.82 (d, J = 46.8 Hz).

IR (neat, ν/cm^{-1}) 2949, 2868, 1728, 1504, 1490, 1237, 1039, 936, 810.

HRMS (ESI^+): $[M+H]^+$ cal'd for $C_{15}H_{17}F_2O_2$: 267.1191 found: 267.1171.

1-bromo-4-(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (68)[48]

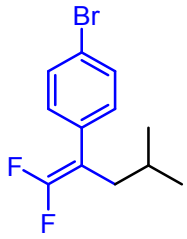


Compound **68** was prepared according to the general procedure (GP2) and isolated as oil.

Column Chromatography : Silica, Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (m, 2H), 7.18 (m, 2H), 2.24 (dt, J = 7.1, 2.4 Hz, 2H), 1.62-1.54 (m, 5H), 1.26-1.15 (m, 4H), 0.90-0.85 (m, 2H). Spectroscopic data were consistent with literature values.

1-bromo-4-(1,1-difluoro-4-methylpent-1-en-2-yl)benzene (69)[48]

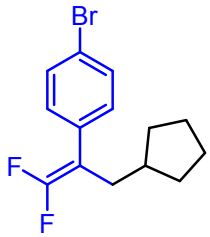


Compound **69** was prepared according to the general procedure (GP2) and isolated as oil.

Column Chromatography : Silica, Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 7.22 – 7.12 (m, 2H), 2.25 (ddd, J = 7.5, 4.9, 2.8 Hz, 2H), 1.62 – 1.50 (m, 1H), 0.88 (d, J = 6.7 Hz, 6H). Spectroscopic data were consistent with literature values.

1-bromo-4-(3-cyclopentyl-1,1-difluoroprop-1-en-2-yl)benzene (70)



Compound **70** was prepared according to the general procedure (GP2) and isolated as oil.

Column Chromatography : Silica, Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 2H), 7.21 – 7.16 (m, 2H), 2.39 – 2.35 (m, 2H), 1.83 – 1.74 (m, 1H), 1.69 – 1.58 (m, 4H), 1.52 – 1.42 (m, 2H), 1.20 – 1.08 (m, 2H).

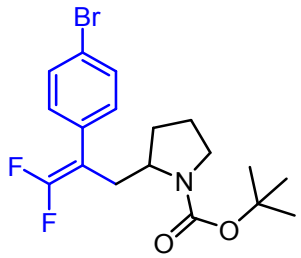
^{13}C NMR (75 MHz, $CDCl_3$) δ 153.94 (dd, J = 290.3, 286.7 Hz), 133.13 (dd, J = 4.6, 2.8 Hz), 131.69, 130.15 (t, J = 3.2 Hz), 121.23, 91.78 (dd, J = 22.5, 12.7 Hz), 38.35 (t, J = 2.2 Hz), 33.53, 32.26, 25.10.

^{19}F NMR (376 MHz, $CDCl_3$) δ -91.18 (d, J = 43.4 Hz), -91.59 (d, J = 43.4 Hz).

IR (neat, ν/cm^{-1}) 2949, 2866, 1723, 1488, 1450, 1237, 1155, 1098, 824, 741, 580, 502.

HRMS (ESI^+): $[M+H]^+$ cal'd for $C_{14}H_{16}BrF_2$: 301.0398 found: 301.0757.

tert-butyl 2-(2-(4-bromophenyl)-3,3-difluoroallyl)pyrrolidine-1-carboxylate(71)



Compound **71** was prepared according to the general procedure (GP2) and isolated as viscous oil.

Column Chromatography : Silica, gradient 0-10 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.26 (br m, 2H), 3.78 (br m, 1H), 3.30 (br m, 2H), 3.00 – 2.77 (m, 1H), 2.46-2.33 (m, 1H), 1.90 – 1.71 (m, 3H), 1.67 – 1.58 (m, 1H), 1.45 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ **156.56, 154.62, 154.49, 152.71, 152.66**, 132.16, 131.78, 129.90, **121.51, 121.32**, **89.72**, 79.75, 79.15, 55.53, **46.78, 46.39**, 31.57, 30.71, 29.82, **29.63**, **28.69**, 23.68, **22.74**.

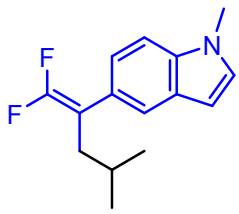
^{19}F NMR (376 MHz, $CDCl_3$) δ -89.00 (q, J = 38.4 Hz), -89.48 (s).

IR (neat, ν/cm^{-1}) 2967, 1687, 1490, 1364, 1343, 1246, 1160, 1099, 828, 814, 768.

HRMS (ESI^+): $[M+Na]^+$ cal'd for $C_{18}H_{22}BrF_2NNaO_2$: 424,0699 found: 424.0691.

Note: Due to rotameric carbon, the coupling constant between fluorine and carbon could not be analyzed.

5-(1,1-difluoro-4-methylpent-1-en-2-yl)-1-methyl-1*H*-indole (72)[9]



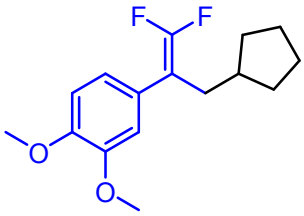
Compound **72** was prepared according to the general procedure (GP2).

Column Chromatography : Silica, gradient 0-4 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.31 (d, J = 8.5 Hz, 1H), 7.18 (dt, J = 8.5, 1.5 Hz, 1H), 7.06 (d, J = 3.1 Hz, 1H), 6.49 (dd, J = 3.1, 0.8 Hz, 1H), 3.80 (s, 3H), 2.33 (ddd, J = 7.3, 2.8,

2.0 Hz, 2H), 1.61 (dt, *J* = 13.7, 6.8 Hz, 1H), 0.90 (d, *J* = 6.7 Hz, 6H). Spectroscopic data were consistent with literature values.

4-(3-cyclopentyl-1,1-difluoroprop-1-en-2-yl)-1,2-dimethoxybenzene (73)



Compound **73** was prepared according to the general procedure (GP2).

Column Chromatography : Silica, gradient 0-4 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 – 6.81 (m, 3H), 3.88 (s, 6H), 2.35 (dt, *J* = 7.5, 2.4 Hz, 2H), 1.81 (dt, *J* = 15.2, 7.6 Hz, 1H), 1.68 – 1.64 (m, 3H), 1.62 – 1.59 (m, 2H), 1.47 (dd, *J* = 7.3, 4.6 Hz, 1H), 1.19 – 1.09 (m, 2H).

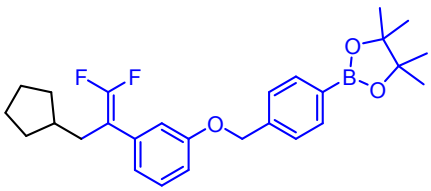
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.92 (dd), 148.85 , 148.29 , 126.68 (d, *J* = 2.2 Hz), 120.95 (t, *J* = 2.9 Hz), 111.87 (t, *J* = 3.3 Hz), 111.12 , 92.17 (dd, *J* = 19.9, 15.2 Hz), 56.07 , 55.97 , 38.40 (t, *J* = 2.3 Hz), 33.92 , 32.29 , 25.12 .

^{19}F NMR (376 MHz, $CDCl_3$) δ -92.81, -92.83.

IR (neat, ν/cm^{-1}) 2950, 2867, 1729, 1584, 1516, 1252, 1173, 1027, 908, 729.

HRMS (ESI^+): $[M+H]^+$ cal'd for $C_{16}H_{21}F_2O_2$: 283.1504 found: 283.1506.

2-(4-((3-(3-cyclopentyl-1,1-difluoroprop-1-en-2-yl)phenoxy)methyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(74)



Compound **74** was prepared according to the general procedure (GP2) and isolated as oil.

Column Chromatography : Silica, gradient 0-4 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.20 (m, 1H), 6.91 – 6.84 (m, 3H), 5.09 (s, 2H), 2.33 (dt, *J* = 7.5, 2.4 Hz, 2H), 1.78 – 1.69 (m, 1H), 1.60 – 1.55 (m, 5H), 1.48 – 1.40 (m, 2H), 1.34 (s, 12H), 1.16 – 1.05 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.73 , 153.98 (dd, J = 289.7, 285.9 Hz), 140.19 , 135.56 (dd, J = 4.2, 2.3 Hz), 135.18 , 129.44 , 126.68 , 121.30 (t, J = 3.0 Hz), 115.46 (t, J = 3.1 Hz), 113.61 , 92.38 (dd, J = 21.7, 13.1 Hz), 83.96 , 38.32 (t, J = 2.5 Hz), 33.74 , 32.25 , 25.11 , 25.01 .

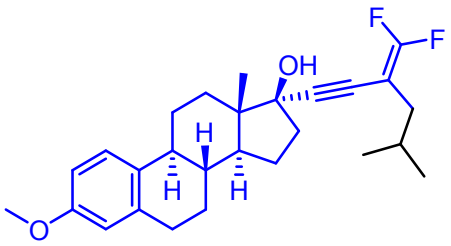
^{19}F NMR (376 MHz, $CDCl_3$) δ -91.73 (d, J = 44.0 Hz), -91.97 (d, J = 44.2 Hz).

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.42.

IR (neat, ν/cm^{-1}) 2948, 2866, 1729, 1611, 1578, 1537, 1339, 1240, 1142, 1114, 858, 656.

HRMS (ESI$^+$): $[M+isopropanol+H]^+$ cal'd for $C30H_{41}BF_2O_4$: 504.3050 found: 504.3291.

(8R,9S,13S,14S,17S)-17-(3-(difluoromethylene)-5-methylhex-1-yn-1-yl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-ol (75)



Compound **75** was prepared according to the general procedure (GP2) isolated as viscous-oil.

Column Chromatography : Silica, gradient 0-10 % EtOAc/Heptane

Note: The product is not stable and should be kept in fridge. Unknown side product could not be separated by column chromatography. The yield was confirmed by NMR.

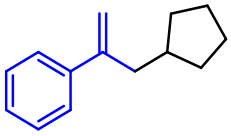
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 9.8 Hz, 1H), 6.71 (dd, J = 8.6, 2.3 Hz, 1H), 6.62 (m, 1H), 3.77 (s, 3H), 2.88 – 2.82 (m, 2H), 2.40 – 2.26 (m, 2H), 2.22-2.13 (m, 1H), 2.08 – 1.98 (m, 2H), 1.95 – 1.91 (m, 1H), 1.91 – 1.63 (m, 6H), 1.54-1.42 (m, 3H), 1.16 – 1.10 (m, 2H), 0.96 – 0.81 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.61 (d, J = 2.43Hz), 138.07, 132.61, 126.49, 113.93, 111.62, δ 96.93 (t, J = 5.6 Hz), 80.47 (d, J = 6.2 Hz), 78.29 (dd, J = 8.3, 4.1 Hz), 55.29, 49.85, 49.79, 47.72, 47.65, 43.99, 43.83, 39.62, 39.30, 39.16, 33.03, 32.97, 32.02, 29.95, 29.16, 27.47, 27.31 (t, J = 2.2 Hz) 26.57, 22.94, 22.83, 19.25, 14.24.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.49 (d, J = 19.0 Hz), -85.45 (d, J = 18.9 Hz).

GC-EI: cal'd for $C_{27}H_{34}F_2O_2$: 428.25, found: 428.15.

(3-cyclopentylprop-1-en-2-yl)benzene(76)



Compound **76** was prepared according to the general procedure (GP1) and isolated as oil.

Column Chromatography : Silica, gradient 0-4 % EtOAc/Heptane

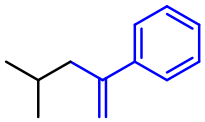
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.3, 1.3 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.22 – 7.16 (m, 1H), 5.17 (d, J = 1.7 Hz, 1H), 4.99 (q, J = 1.2 Hz, 1H), 2.45 (dd, J = 7.4, 0.9 Hz, 2H), 1.86 (hept, J = 7.5 Hz, 1H), 1.67 – 1.59 (m, 2H), 1.56 – 1.52 (m, 3H), 1.46 – 1.36 (m, 1H), 1.15 – 1.03 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.59, 141.78, 128.31, 127.32, 126.40, 112.89, 42.15, 38.33, 32.58, 25.21.

IR (neat, ν/cm^{-1}) 2947, 2864, 1626, 1446, 892, 776, 699.

HRMS (APCI): $[M+H]^+$ cal'd for $C_{14}H_{19}$: 187.1481 found: 187.1264

(4-methylpent-1-en-2-yl)benzene (**77**)[50]

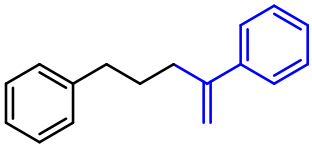


Compound **77** was prepared according to the general procedure (GP1) and isolated as oil.

Column Chromatography : Silica, *iso*-hexane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (m, 5H), 5.28 (s, 1H), 5.05 (s, 1H), 2.41 (d, J = 7.1 Hz, 2H), 1.70 (dt, J = 13.5, 6.7 Hz, 1H), 0.90 (d, J = 6.6 Hz, 6H). Spectroscopic data were consistent with literature values.

pent-4-ene-1,4-diyldibenzene (78)[51]



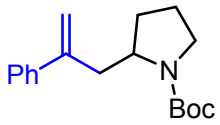
Compound **78** was prepared according to the general procedure (GP1) and isolated as oil.

Column Chromatography : Silica, gradient 0-4 % EtOAc/Heptane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.33 – 7.29 (m, 1H), 7.31 – 7.18 (m, 4H), 7.16 – 7.11 (m, 3H), 5.27 (d, J = 1.6 Hz, 1H), 5.06 (d, J = 1.6 Hz, 1H), 2.63 (t, J = 7.7 Hz, 2H), 2.53 (t, J = 7.5 Hz, 2H), 1.77 (p, J = 7.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.46, 142.44, 141.42, 128.65, 128.62, 128.58, 128.49, 128.39, 128.33, 128.30, 128.27, 127.45, 126.27, 125.84, 112.57, 35.58, 34.99, 30.01. Spectroscopic data were consistent with literature values.

tert-butyl 2-(2-phenylallyl)pyrrolidine-1-carboxylate(79)[52]

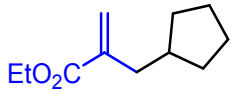


Compound **79** was prepared according to the general procedure (GP1) and isolated as oil.

Column Chromatography : Silica, gradient 0-10 % EtOAc/Heptane

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (br, 2H), 7.38 – 7.26 (m, 3H), 5.37 (d, J = 1.1 Hz, 1H), 5.09 (s, 1H), 3.98-3.86 (br m, 1H), 3.37-3.20 (br m, 3H), 2.42 – 2.22 (m, 1H), 1.92 – 1.71 (m, 4H), 1.54-1.49 (br m, 9H). Spectroscopic data were consistent with literature values.

tert-butyl 2-(2-(ethoxycarbonyl)allyl)pyrrolidine-1-carboxylate (80)[53]

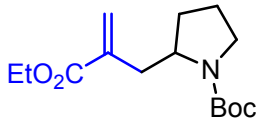


Compound **80** was prepared according to the general procedure (GP1) and isolated as oil.

Column Chromatography : Silica, gradient 0-5 % EtOAc/*iso*-Hexane

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.12 (s, 1H), 5.51 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.30 (d, J = 7.2 Hz, 2H), 2.09 – 1.97 (m, 2H), 1.79 – 1.68 (m, 2H), 1.62 – 1.47 (m, 4H), 1.30 (t, J = 7.1 Hz, 3H), 1.11-1.07 (m, 2H). Spectroscopic data were consistent with literature values.

tert-butyl 2-(2-(ethoxycarbonyl)allyl)pyrrolidine-1-carboxylate (81)



Compound **81** was prepared according to the general procedure (GP1) and isolated as oil.

Column Chromatography : Silica, gradient 5-20 % EtOAc/Heptane

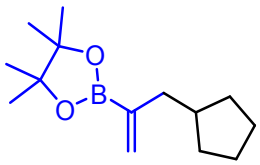
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (d, J = 1.3 Hz, 1H), 5.51 (s, 1H), 4.22 – 4.13 (m, 2H), 3.96 (br s, 1H), 3.33 (br m, 2H), 2.65 (br s, 1H), 2.33 (br s, 1H), 1.87 – 1.75 (m, 3H), 1.66-1.64 (m, 1H), 1.42 (s, 9H), 1.27 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.13, 154.60, 138.37, 127.04, **126.62**, 79.30, 60.73, 56.78, **46.47**, 45.98, 36.57, 35.21, 30.21, 28.56, 22.73, 14.28.

IR (neat, ν/cm^{-1}) 2974, 1715, 1688, 1390, 1364, 1217, 1165, 1142, 770.

HRMS (ESI^+): $[M+Na]^+$ cal'd for $C_{15}H_{25}NNaO_4$: 306.1681 found: 306.1674.

2-(3-cyclopentylprop-1-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (82)[12]



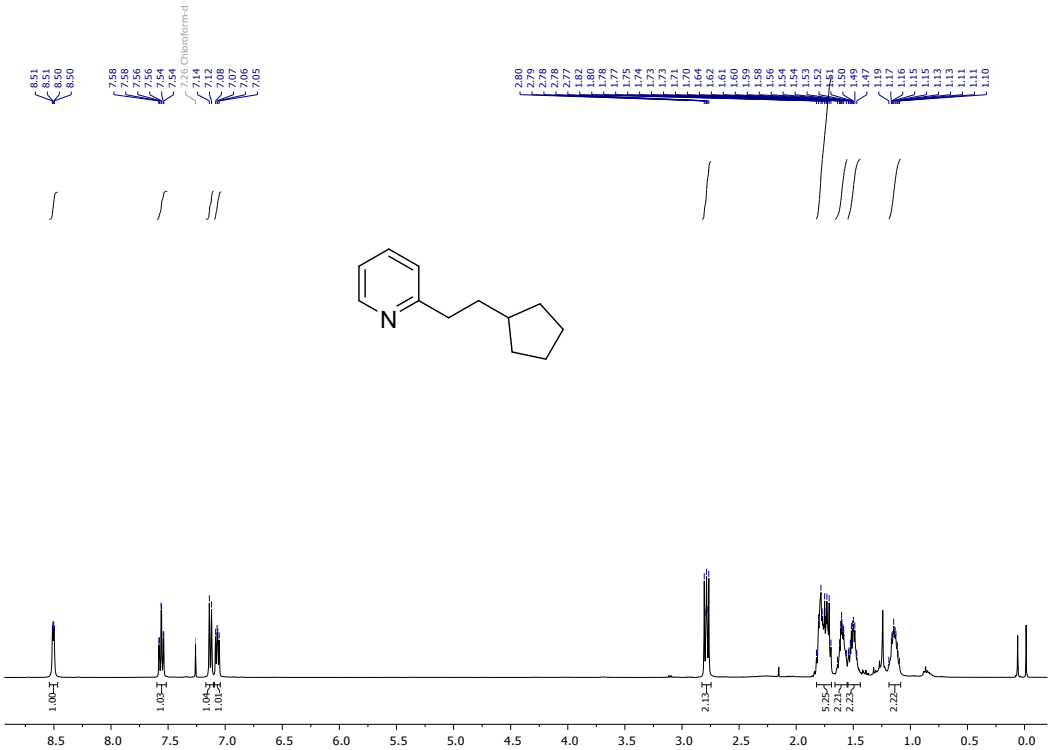
Compound **82** was prepared according to the general procedure (GP1) and isolated as oil.

Column Chromatography : Silica, gradient 0-5 % EtOAc/Heptane

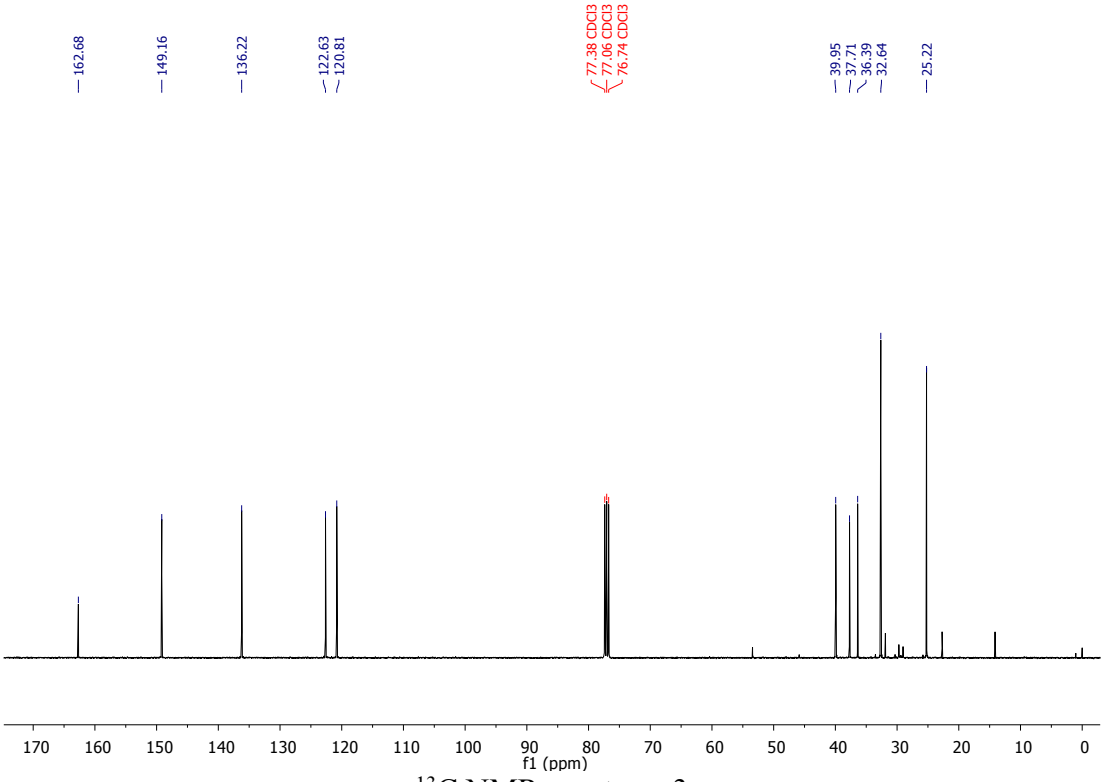
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76 (d, J = 3.3 Hz, 1H), 5.58 (s, 1H), 2.15 (d, J = 7.2 Hz, 2H), 1.97 (dt, J = 15.0, 7.5 Hz, 1H), 1.74-1.65 (m, 2H), 1.61 – 1.53 (m, 2H), 1.52 – 1.44 (m, 2H), 1.26 (s, 12H), 1.17 – 1.03 (m, 2H).

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.26. Spectroscopic data were consistent with literature values.

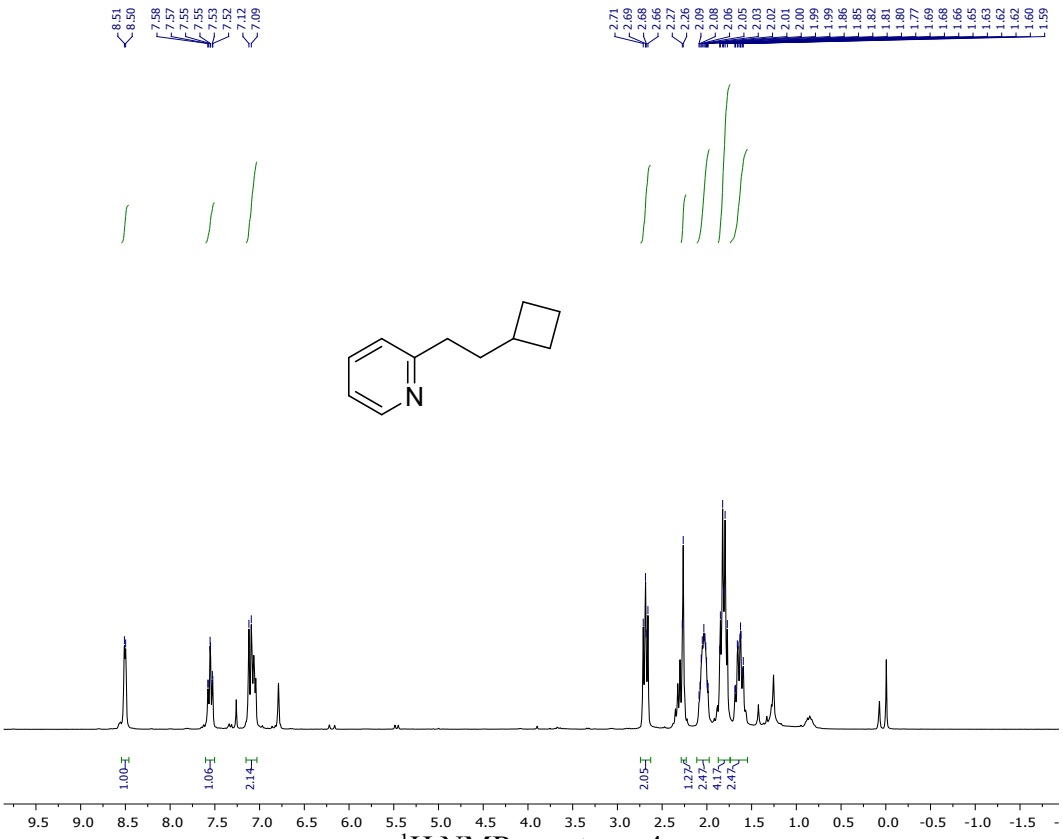
1.7. NMR Spectra



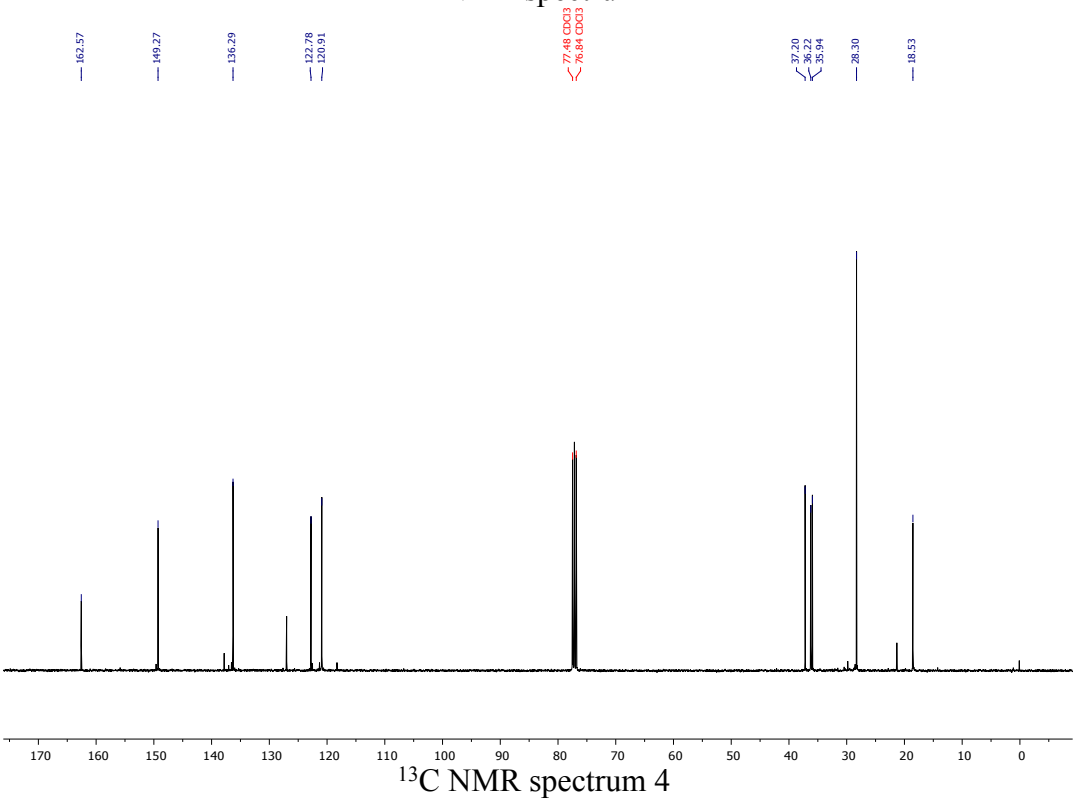
^{1}H NMR spectrum 3



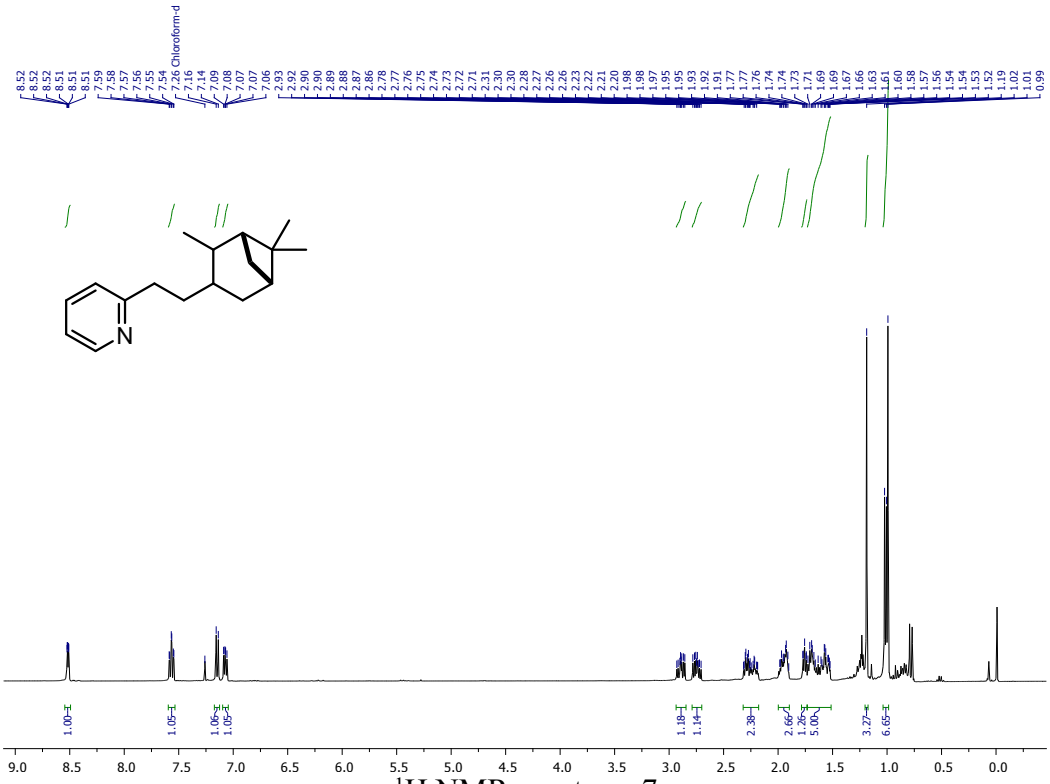
^{13}C NMR spectrum 3



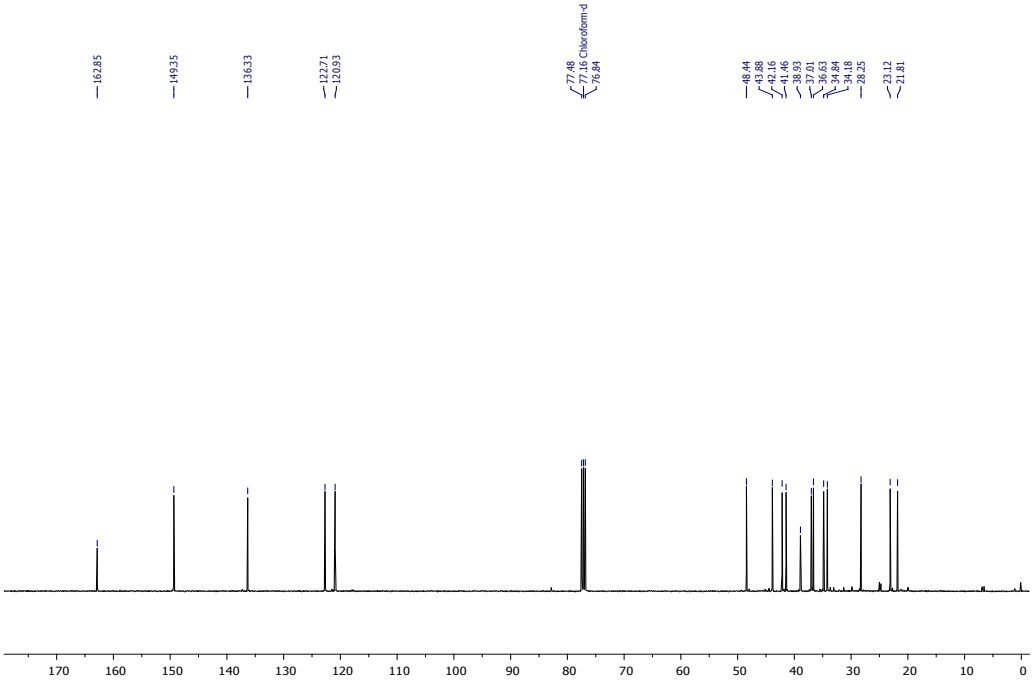
^{1}H NMR spectrum 4



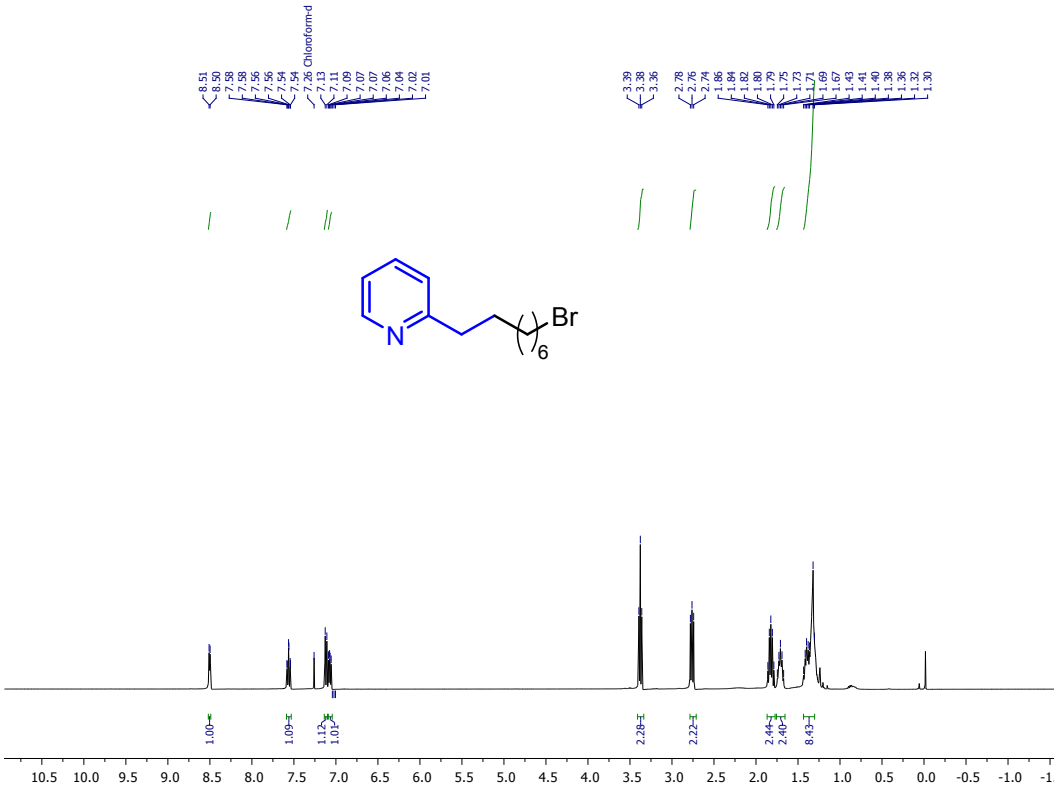
^{13}C NMR spectrum 4



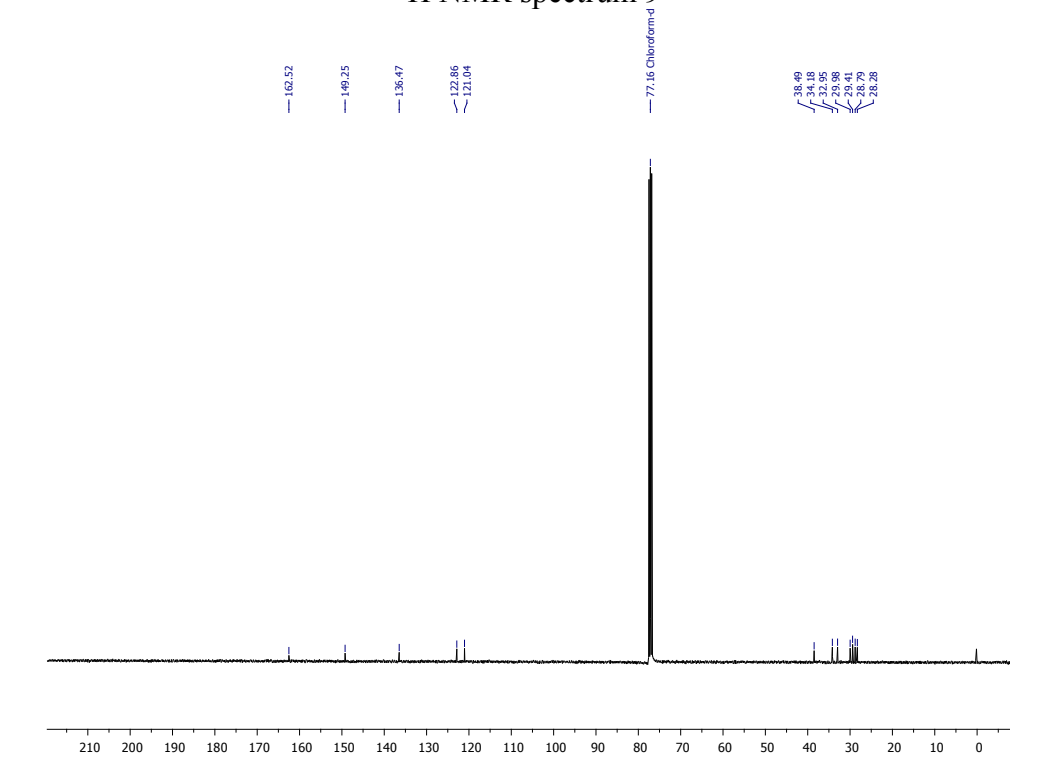
^{1}H NMR spectrum 7



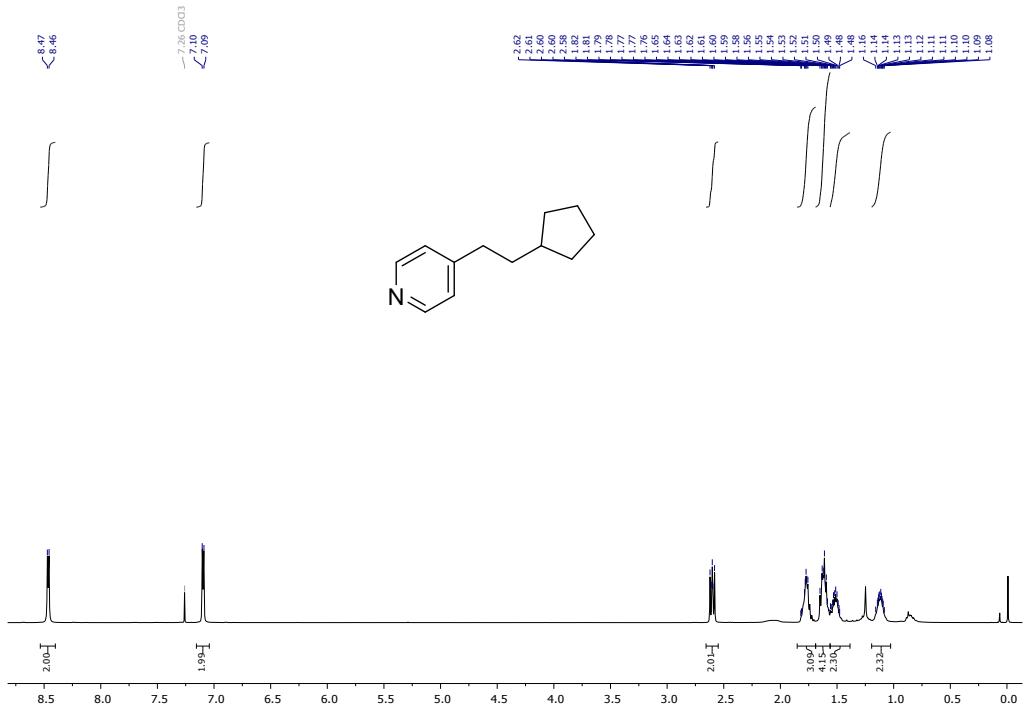
^{13}C NMR spectrum 7



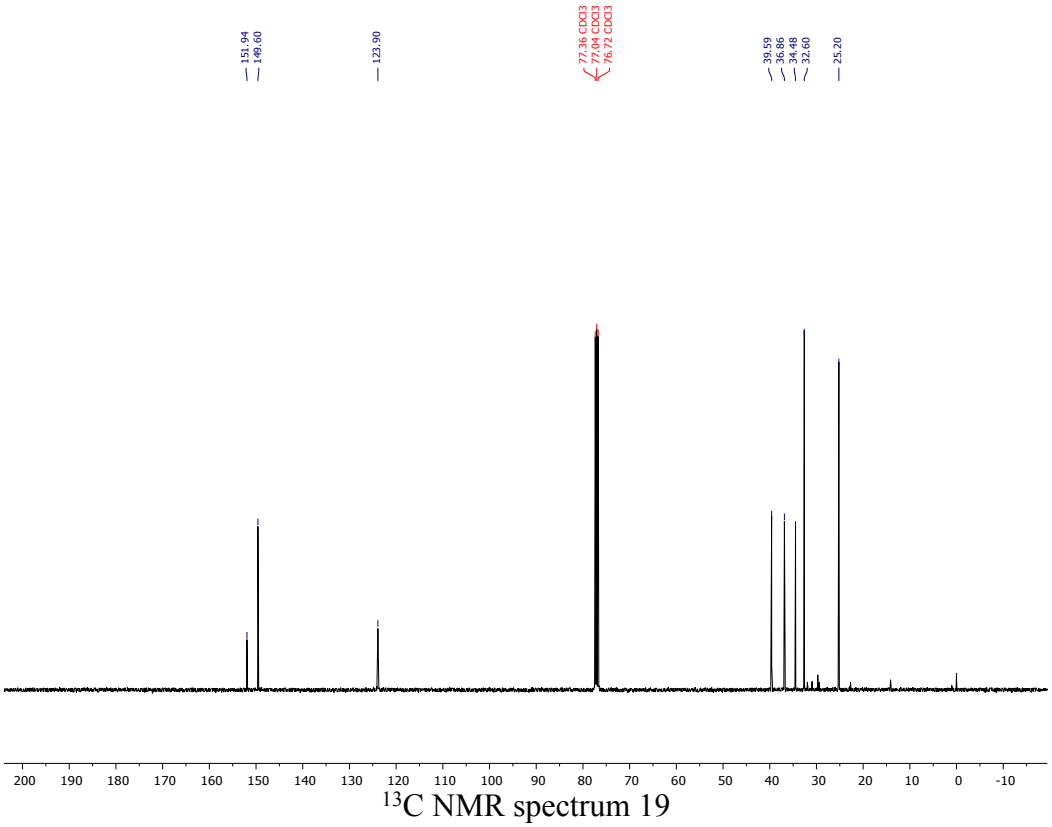
^{1}H NMR spectrum 9



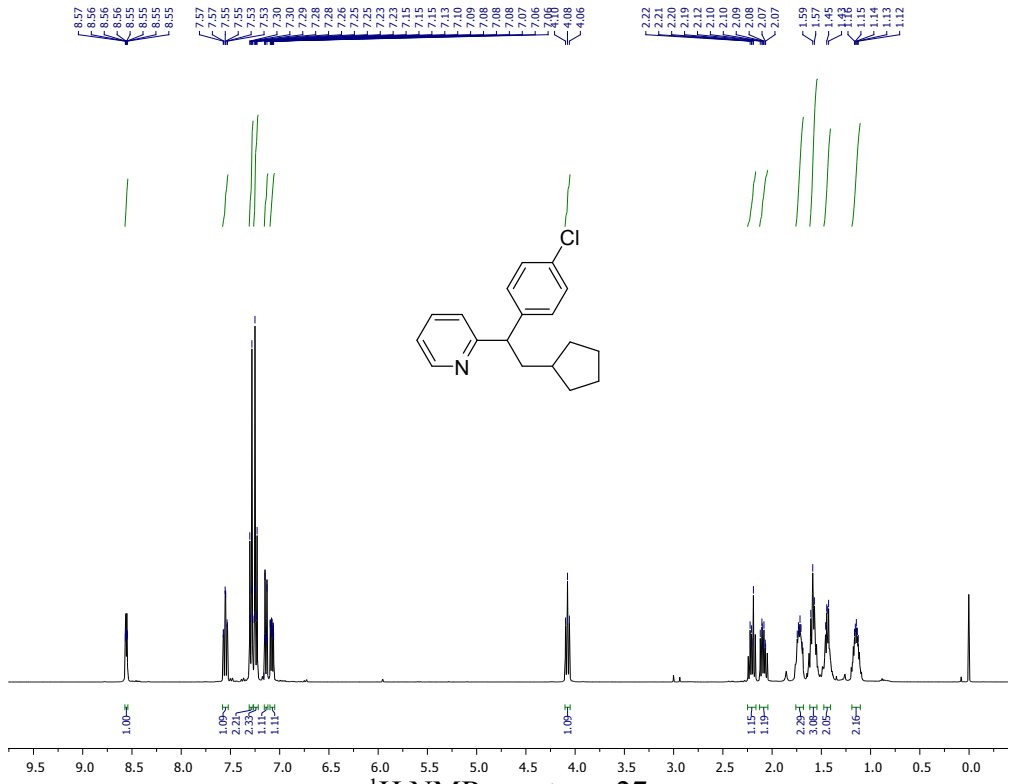
^{13}C NMR spectrum 9



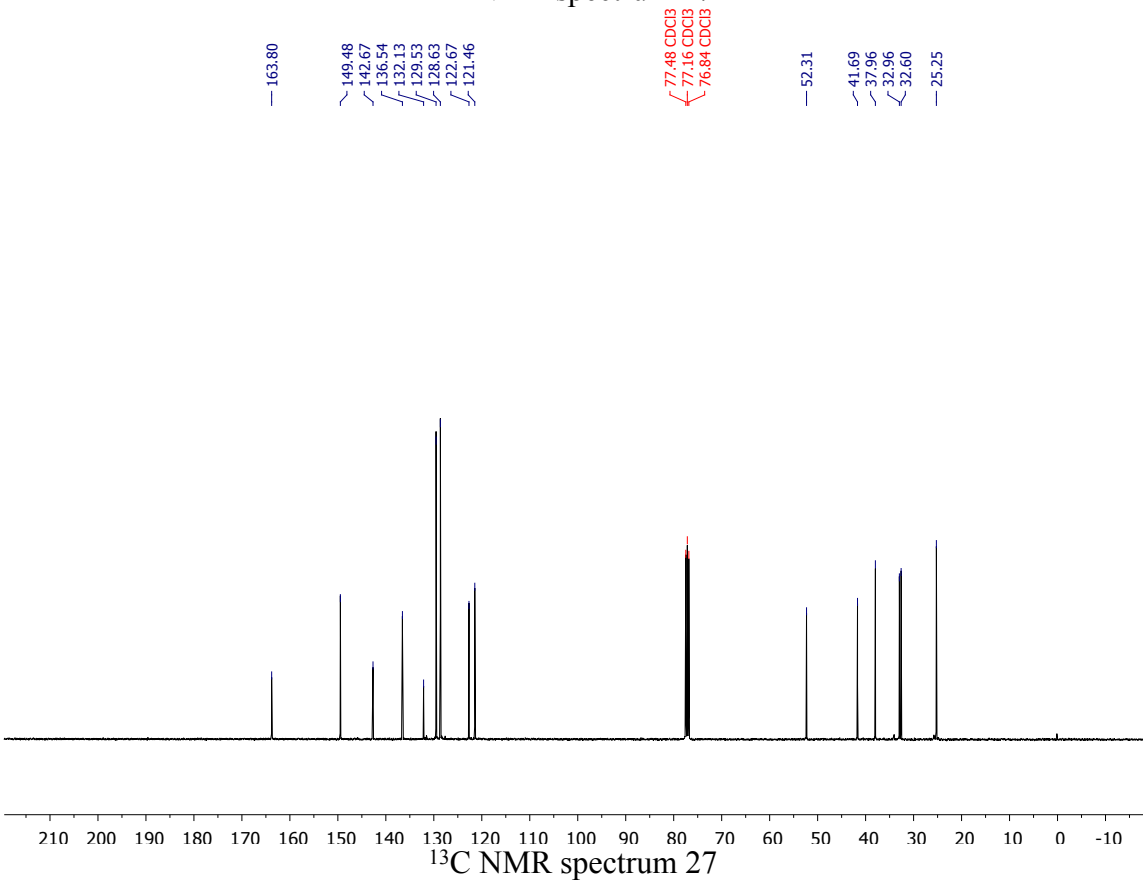
^{1}H NMR spectrum 19



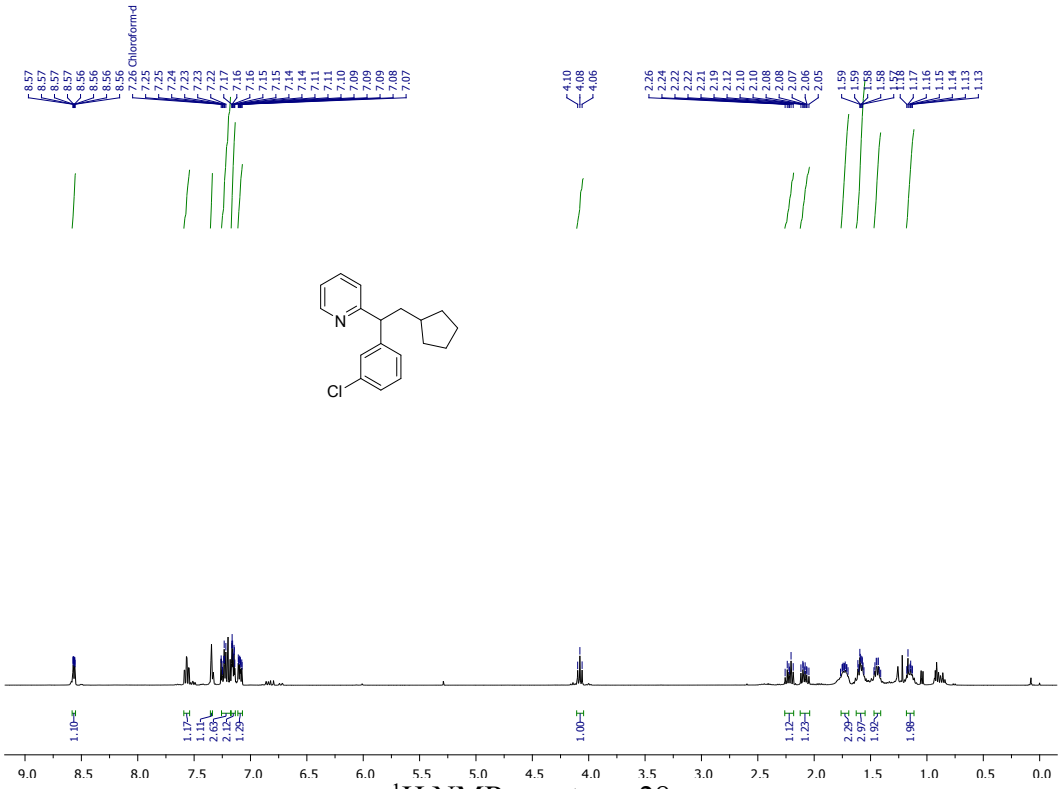
^{13}C NMR spectrum 19



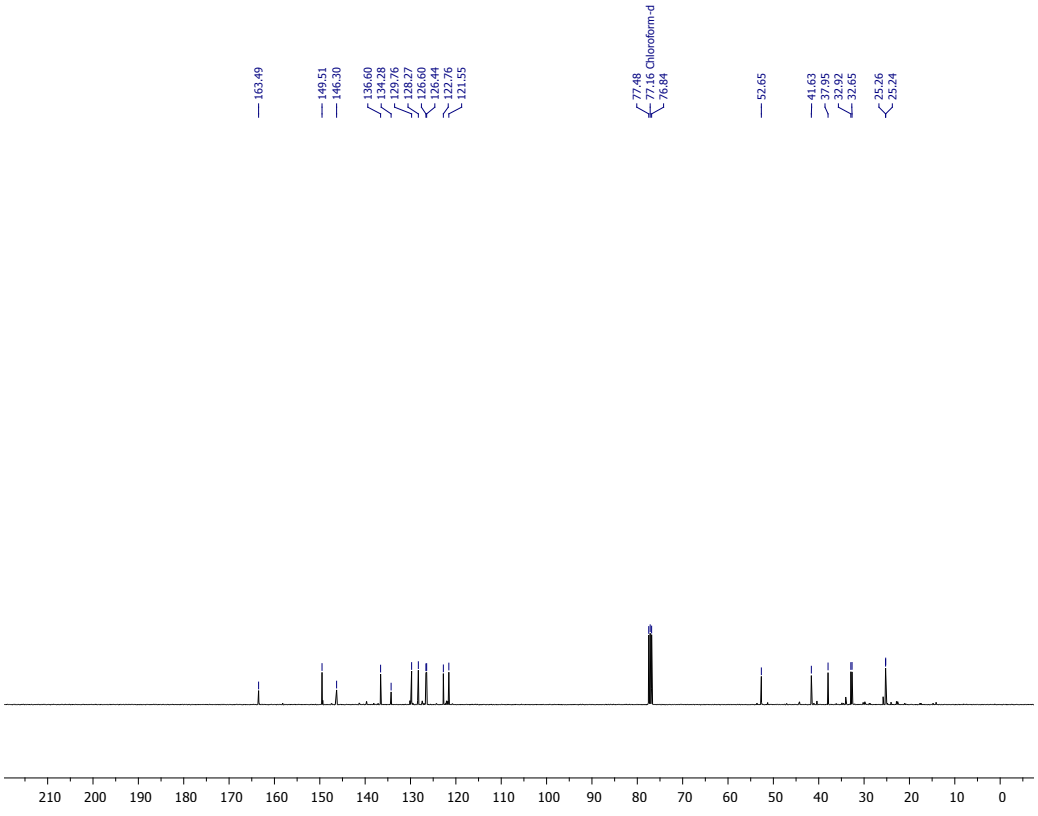
^{1}H NMR spectrum 27



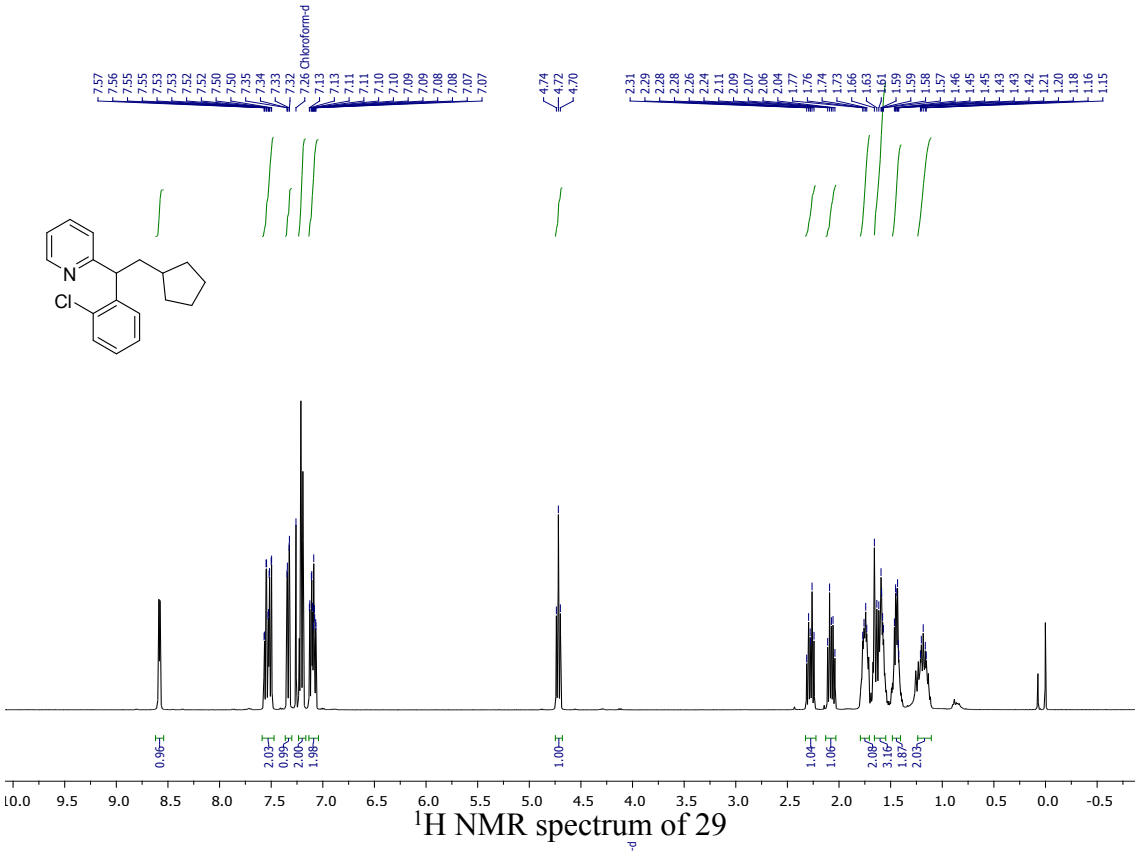
^{13}C NMR spectrum 27



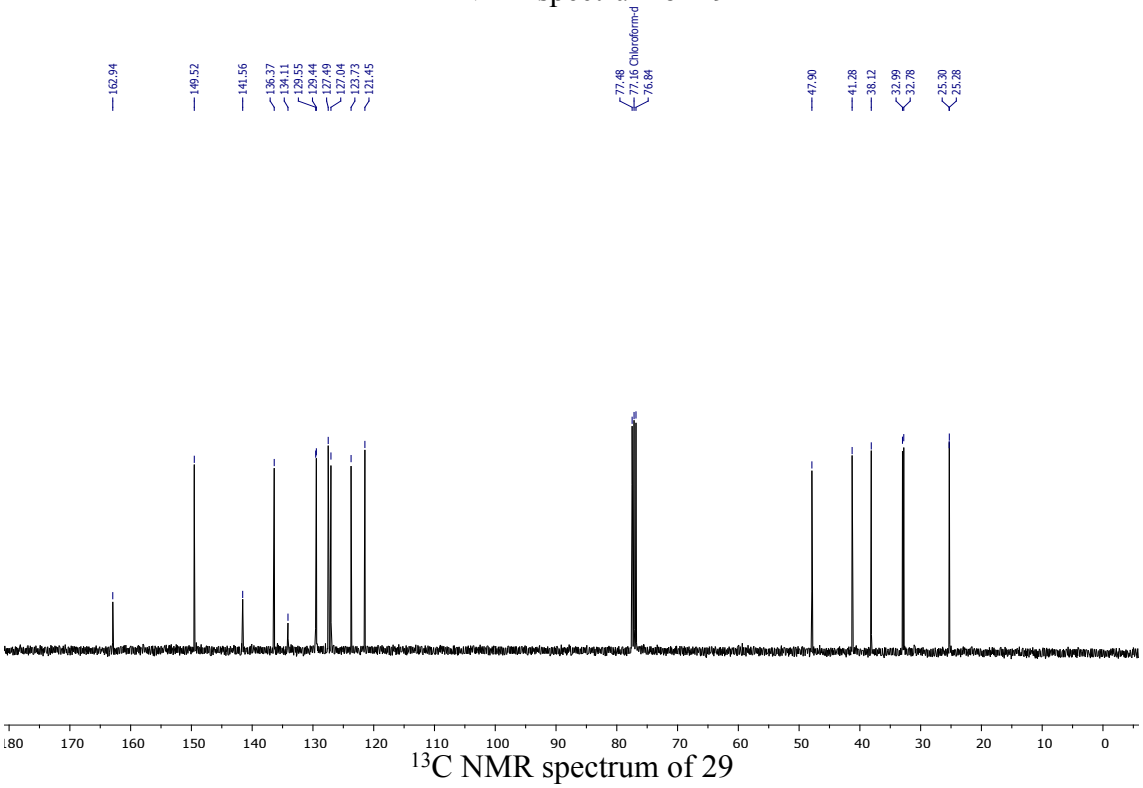
^{1}H NMR spectrum 28



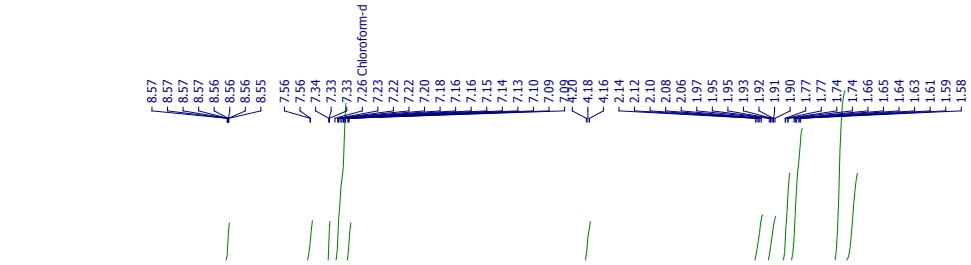
^{13}C NMR spectrum 28

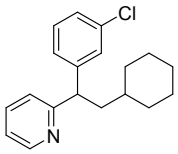


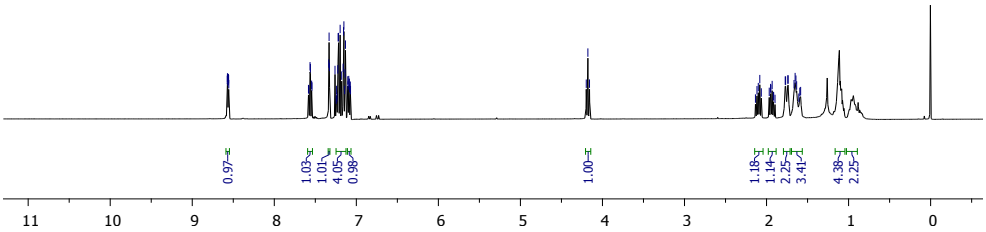
^{1}H NMR spectrum of 29



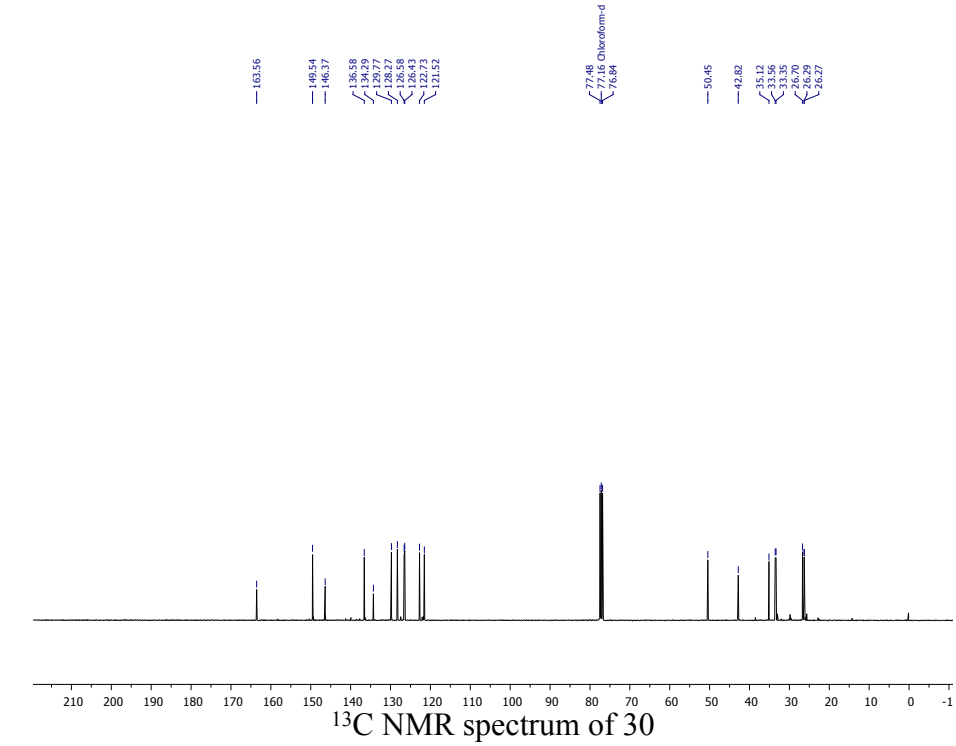
^{13}C NMR spectrum of 29



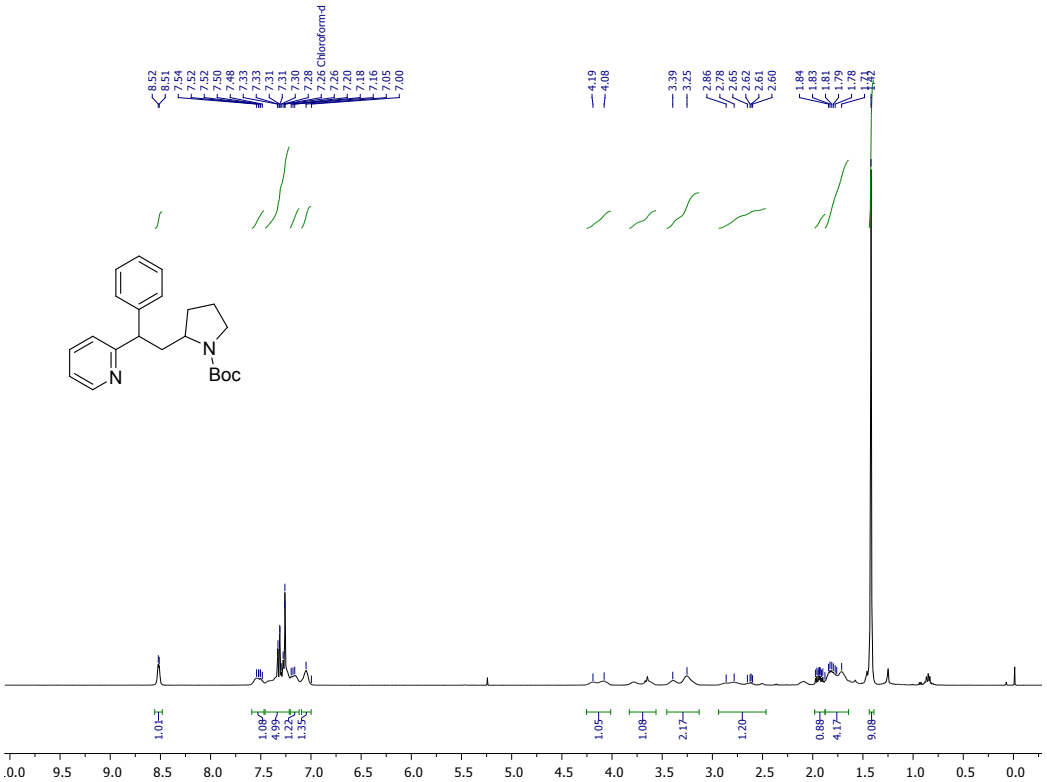




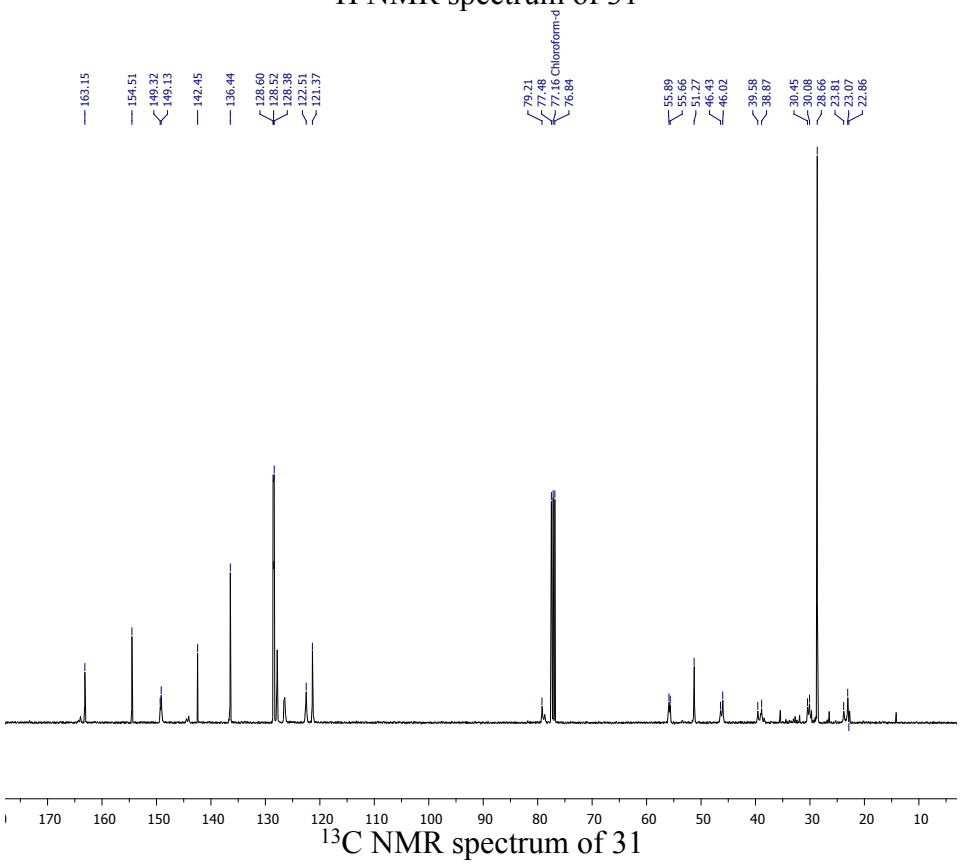
^{1}H NMR spectrum of 30



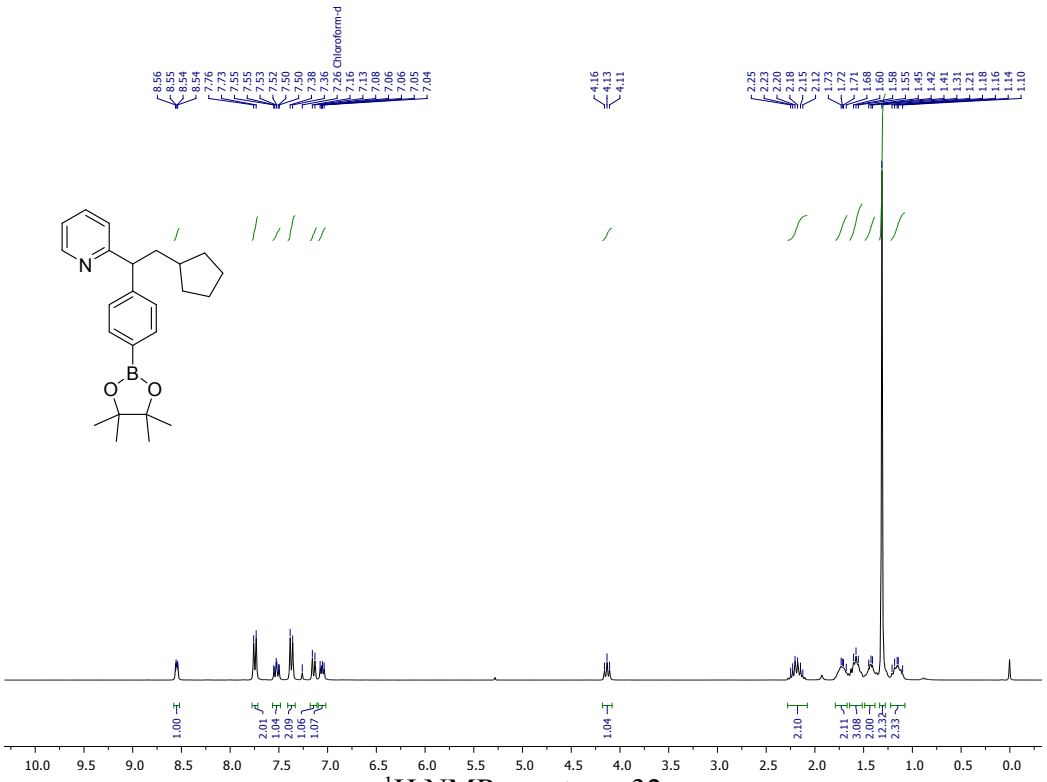
^{13}C NMR spectrum of 30



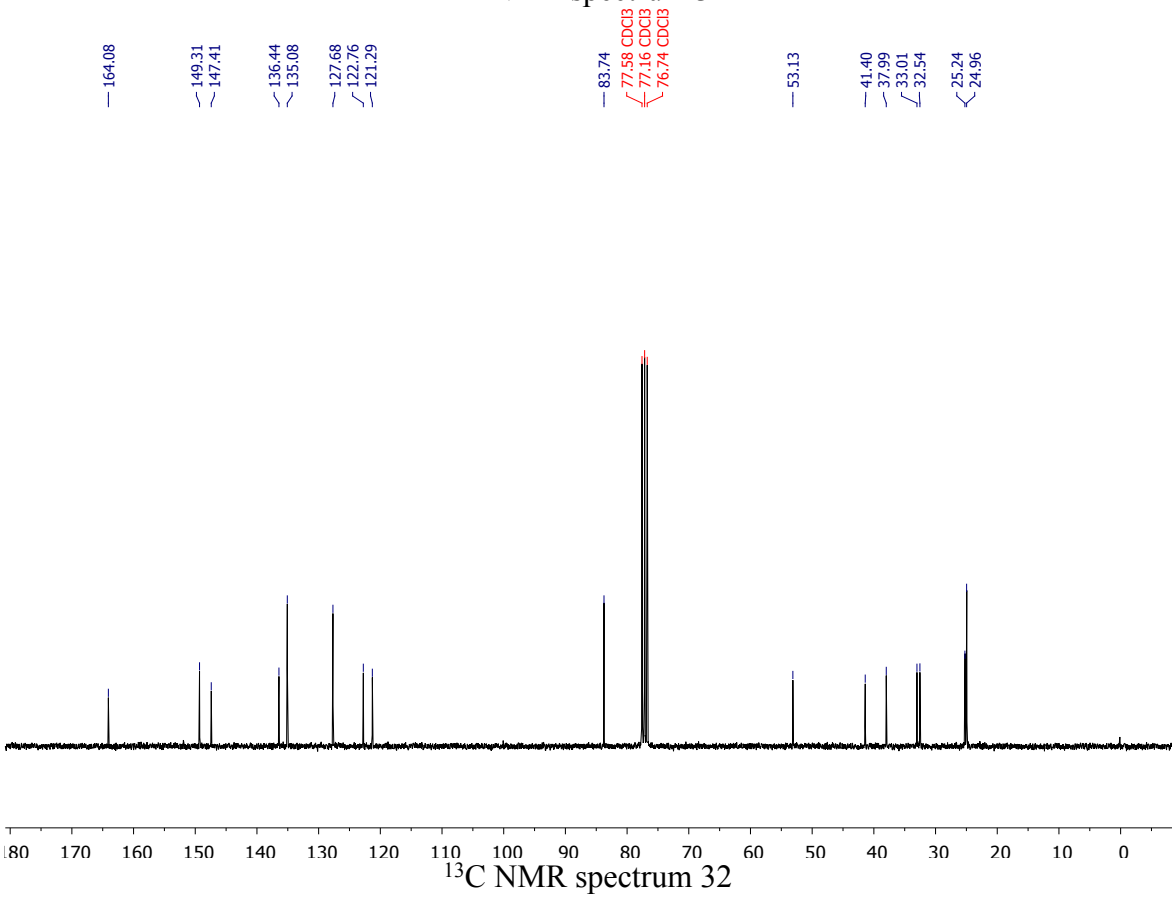
^{1}H NMR spectrum of 31



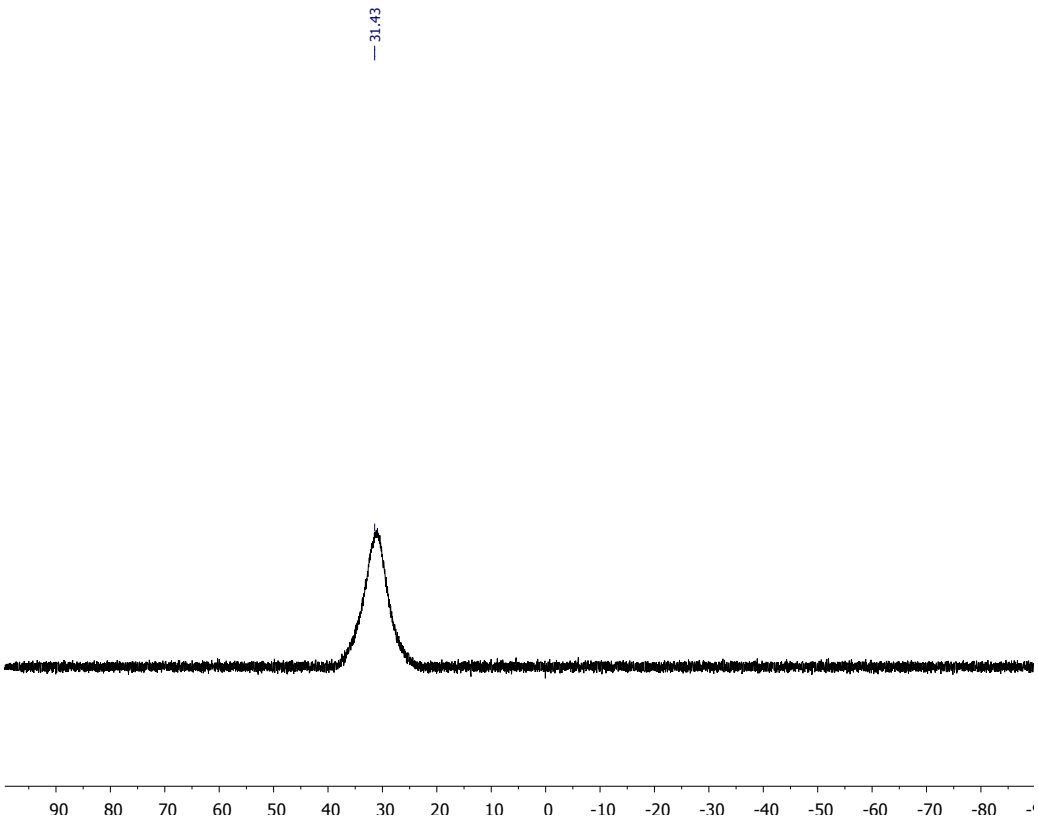
^{13}C NMR spectrum of 31



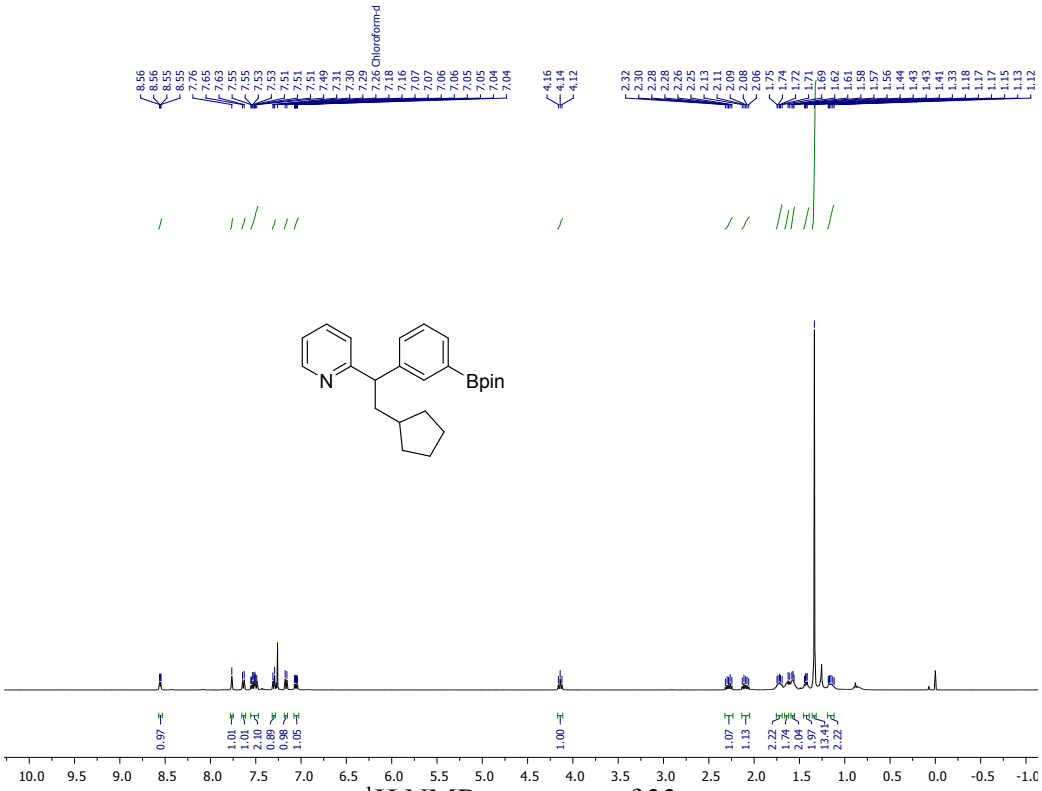
^{1}H NMR spectrum 32



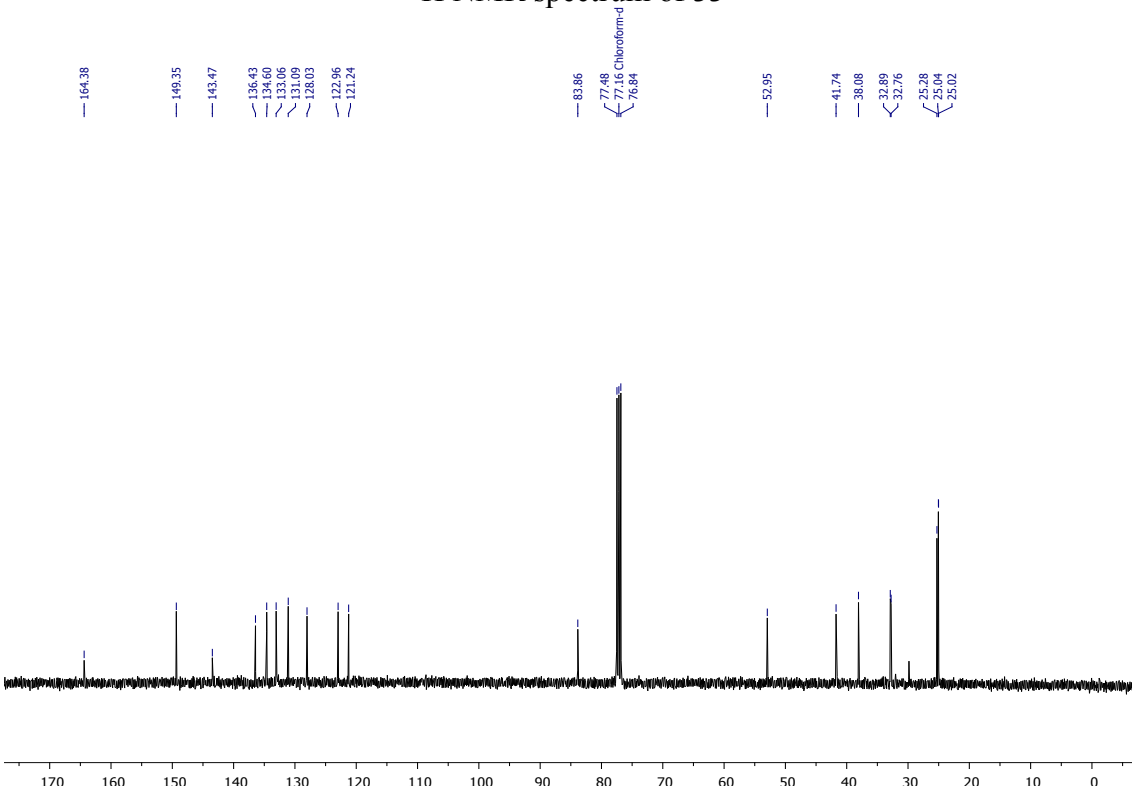
^{13}C NMR spectrum 32



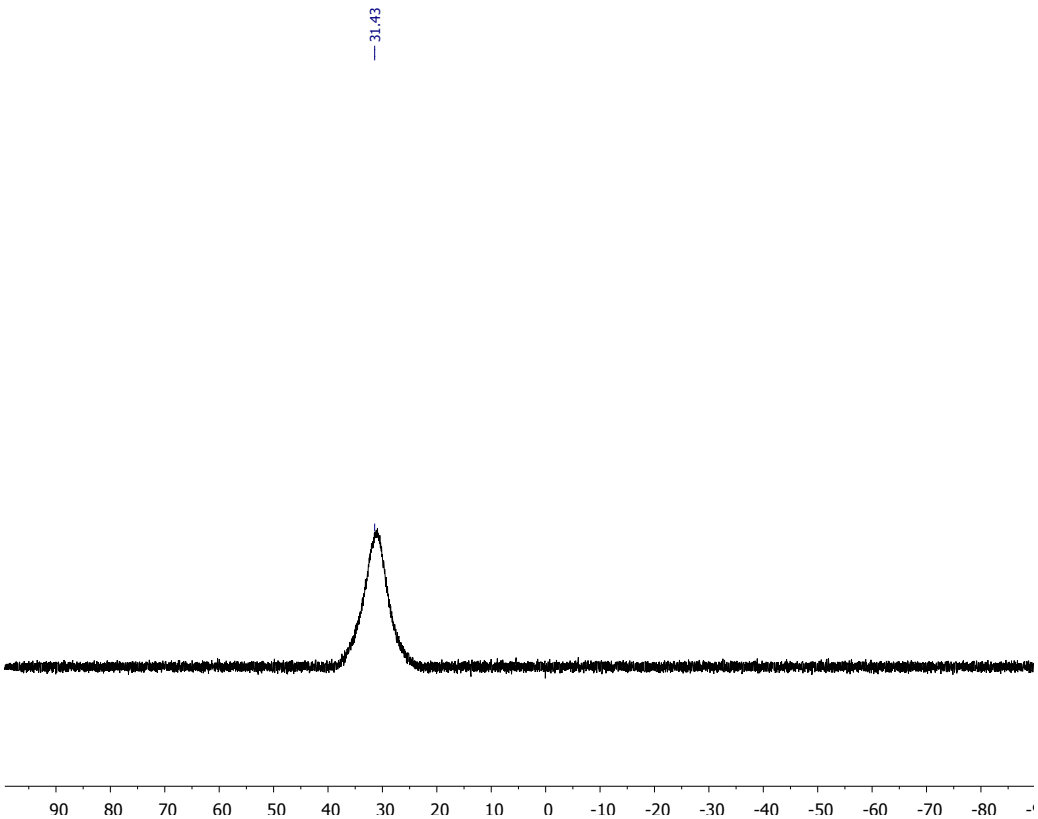
^{11}B NMR spectrum 32



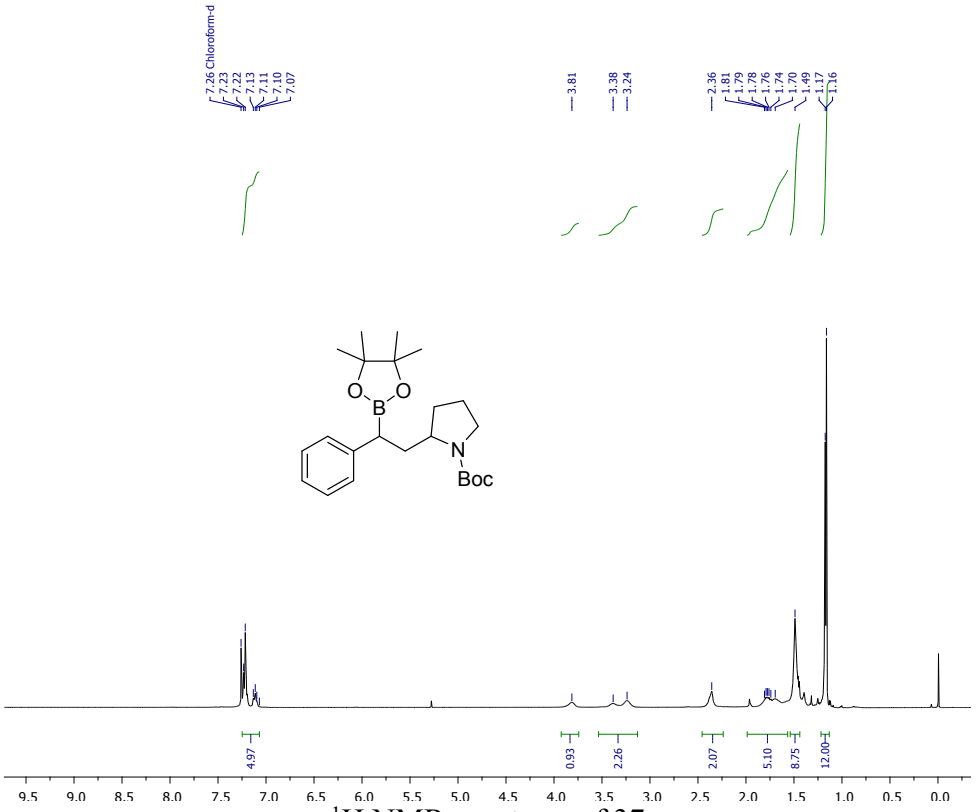
^{1}H NMR spectrum of 33



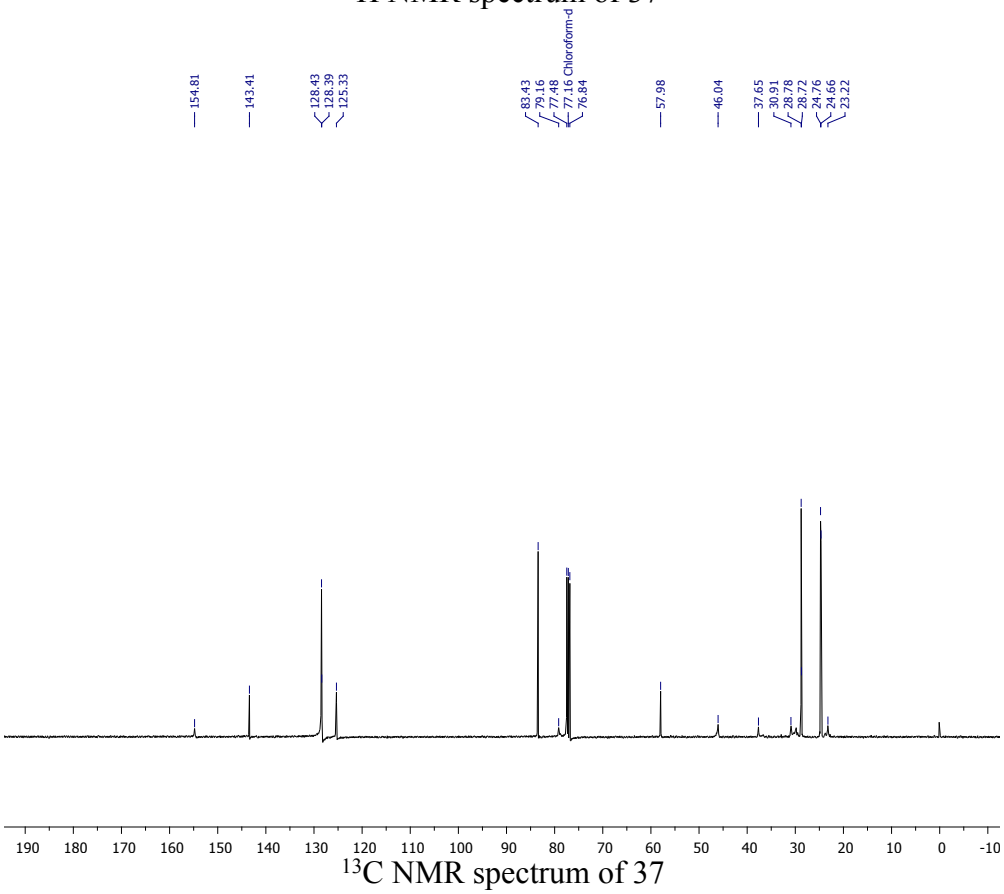
^{13}C NMR spectrum of 33



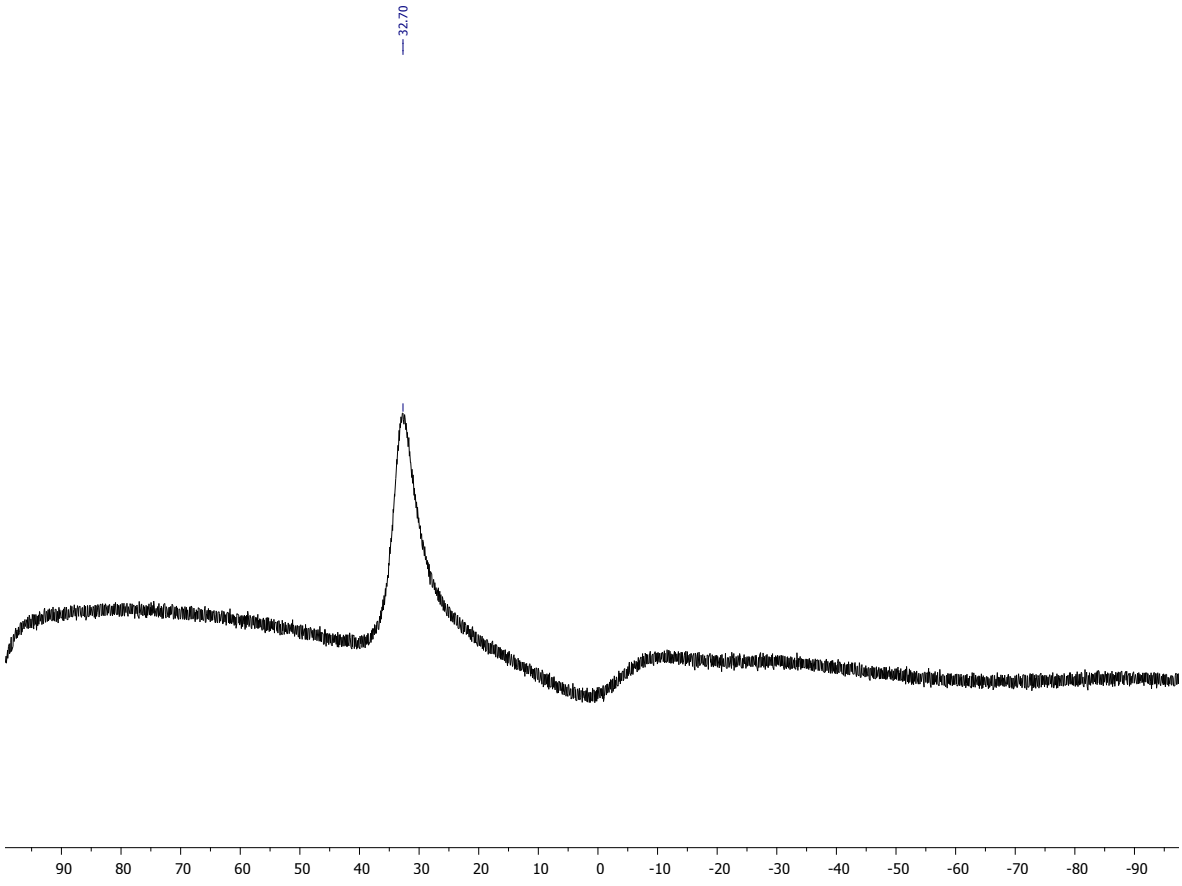
^{11}B NMR spectrum 33



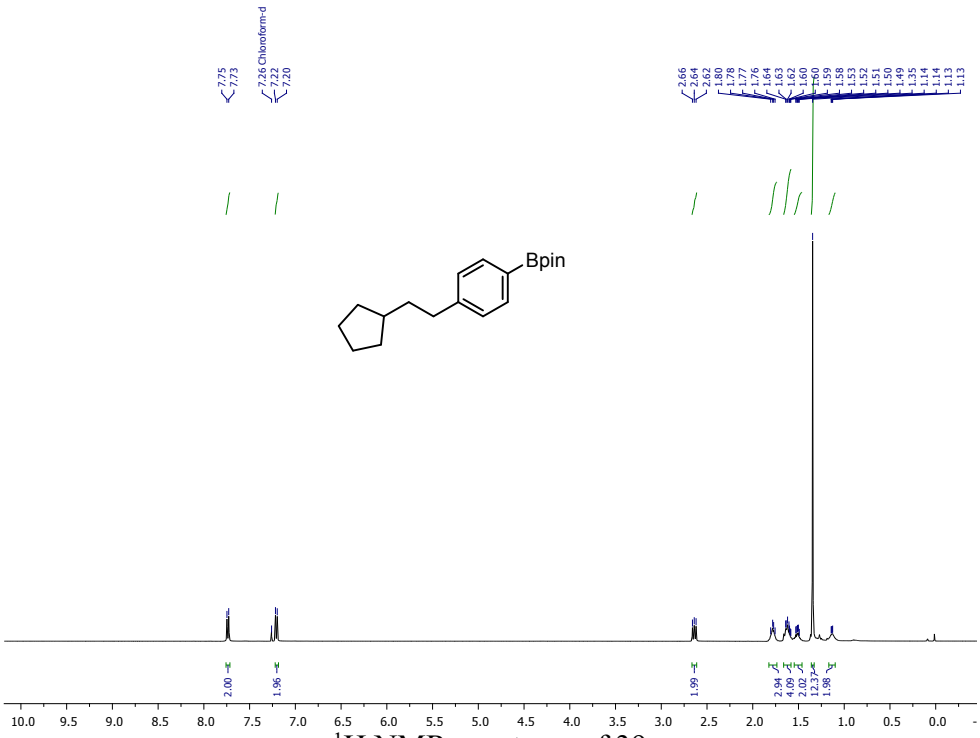
^{1}H NMR spectrum of 37



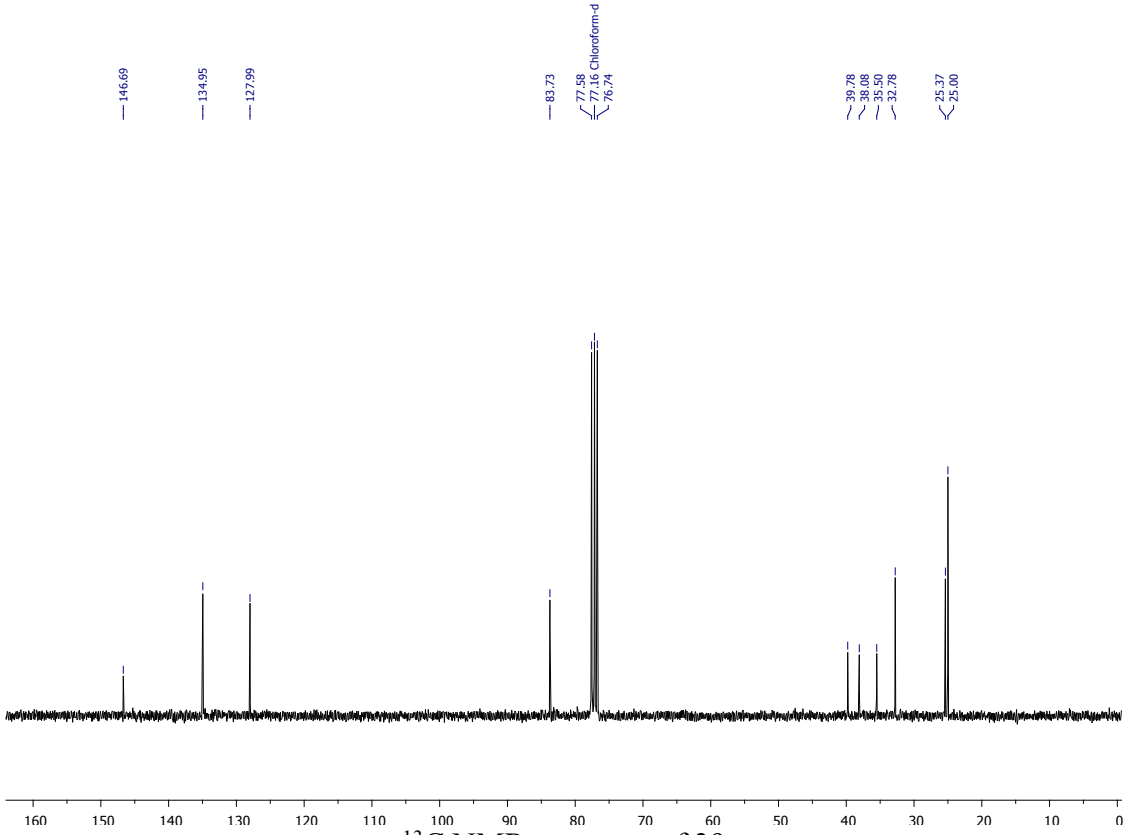
^{13}C NMR spectrum of 37



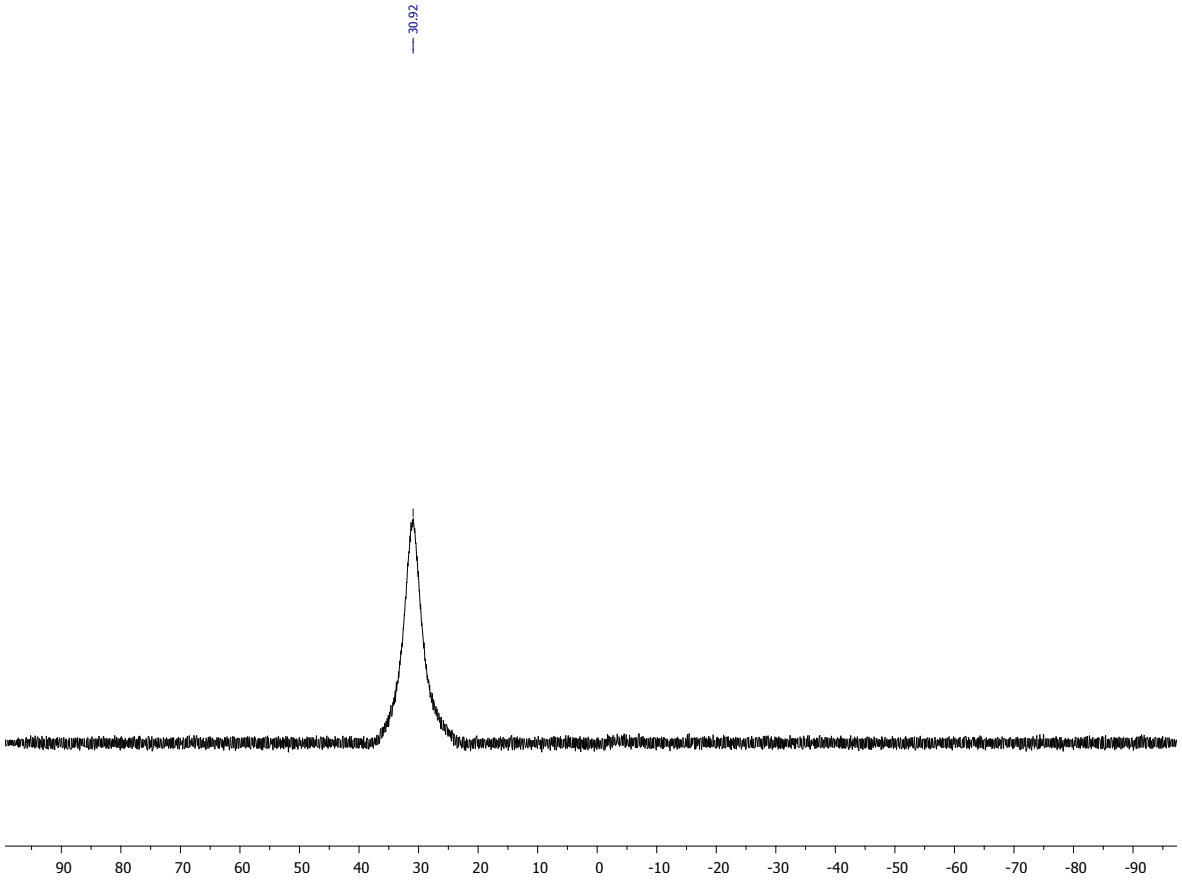
^{11}B NMR spectrum of 37



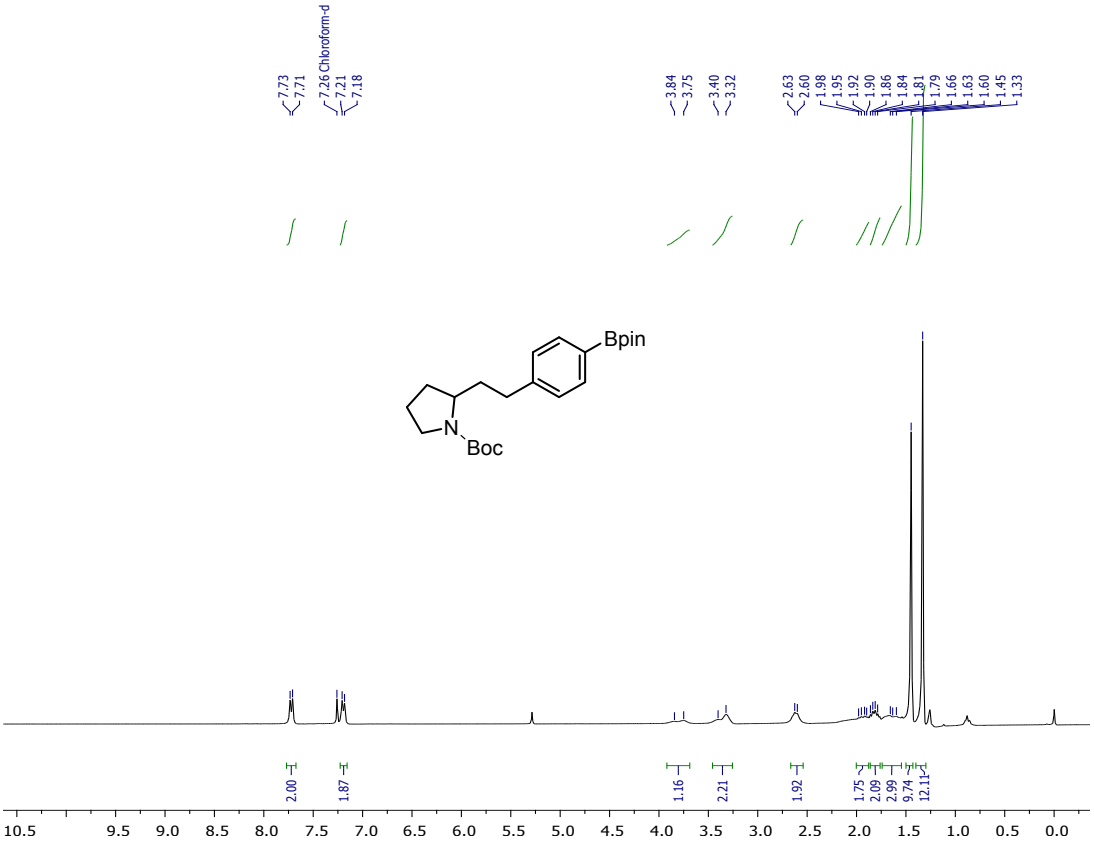
^{1}H NMR spectrum of 39



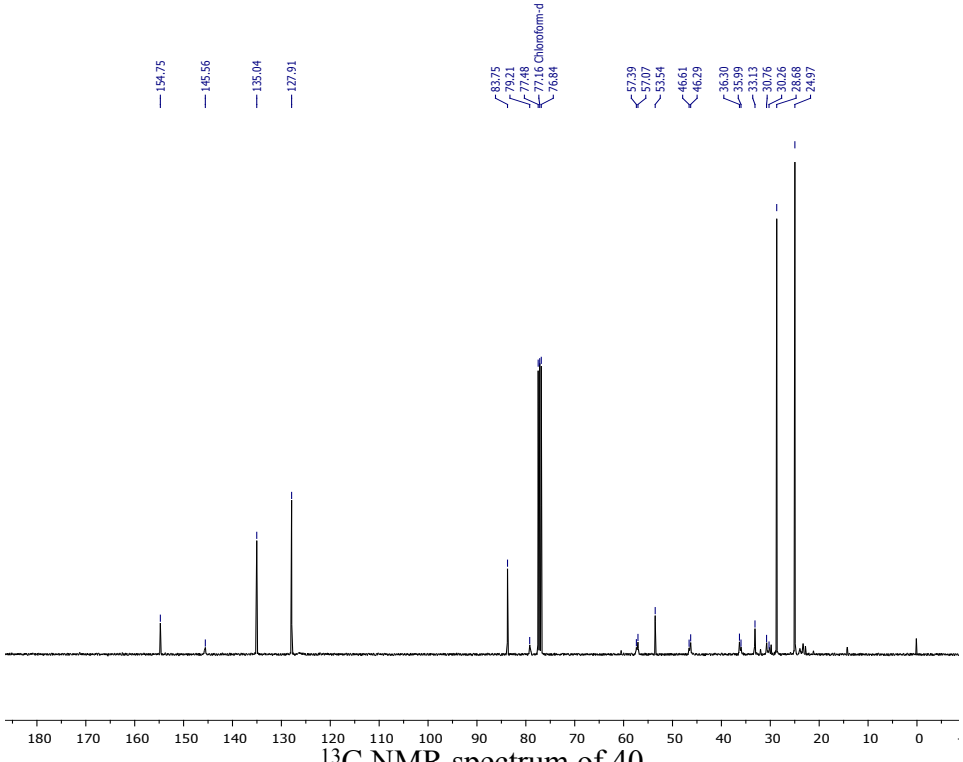
^{13}C NMR spectrum of 39



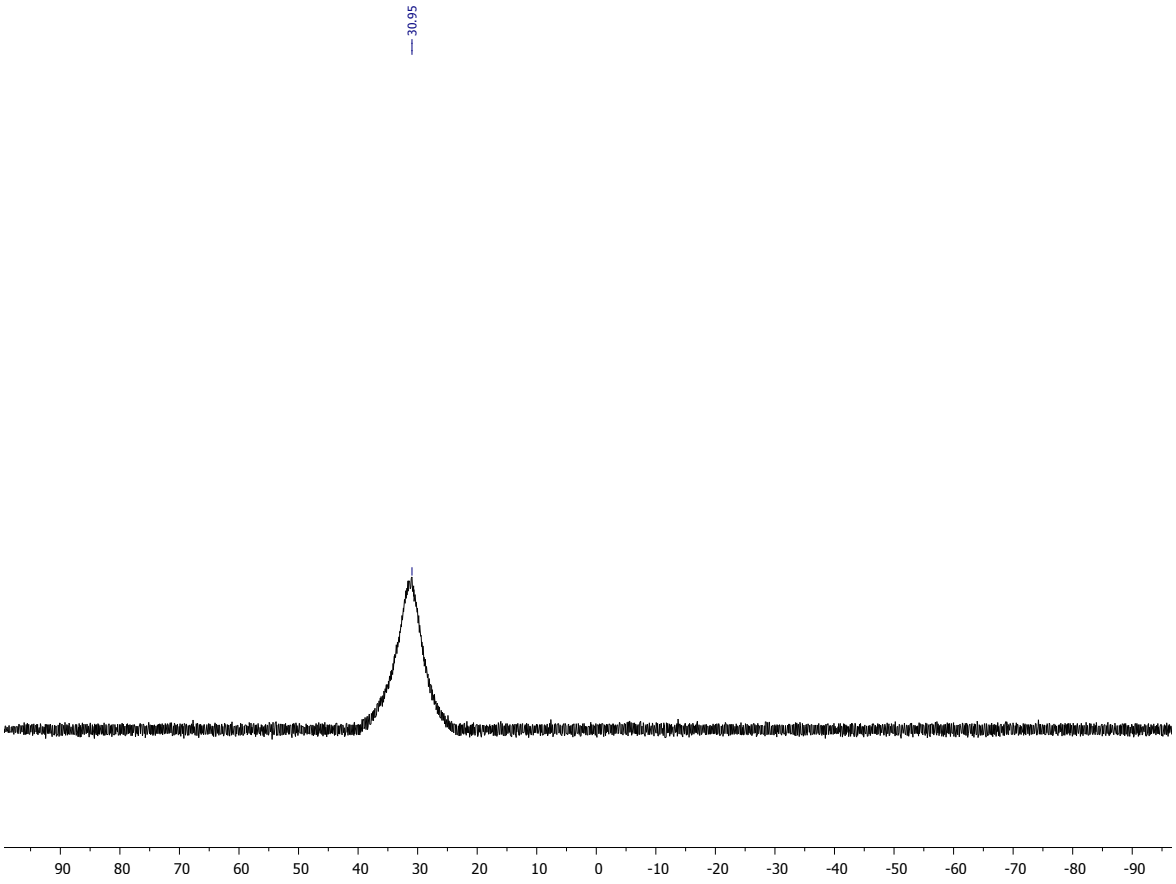
^{11}B NMR spectrum of 39



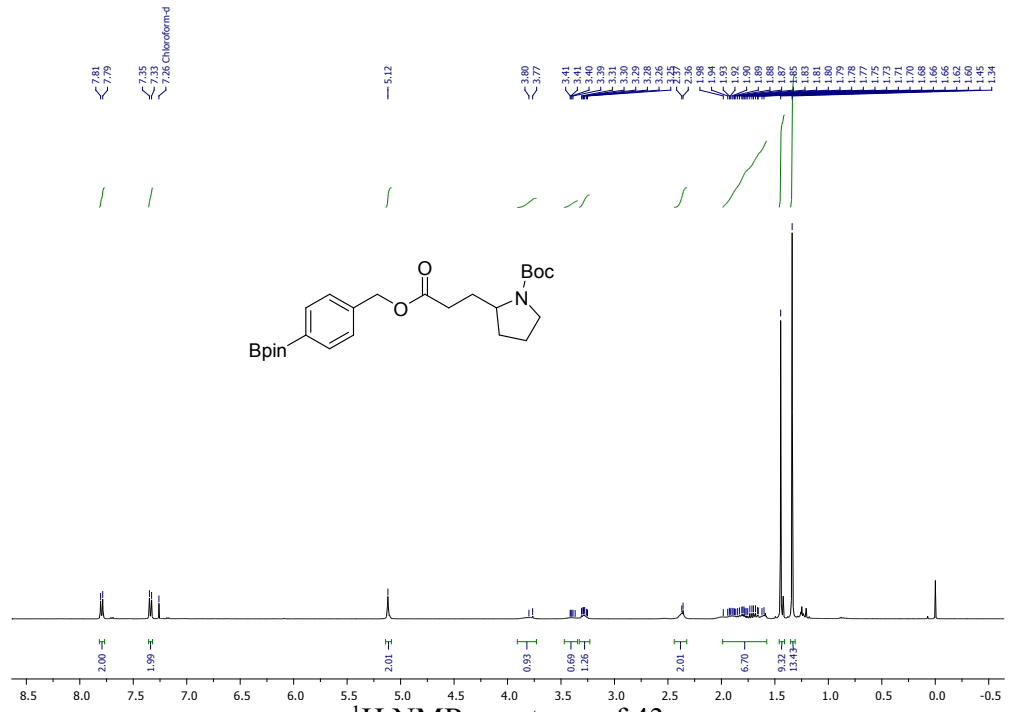
^{1}H NMR spectrum of 40



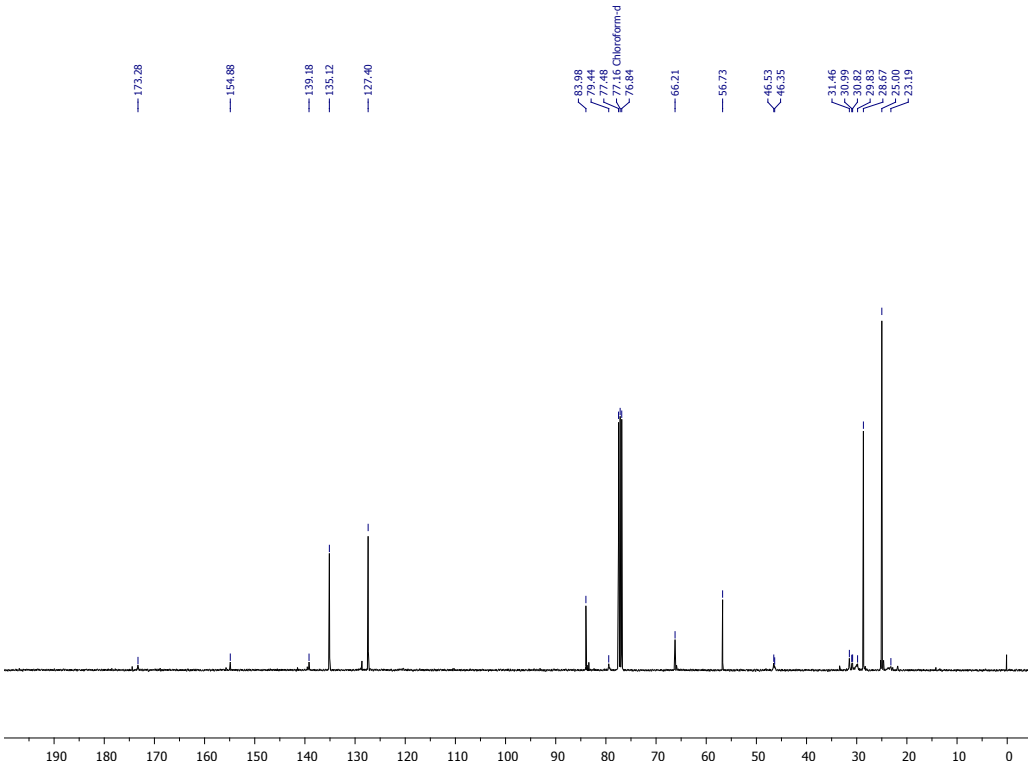
^{13}C NMR spectrum of 40



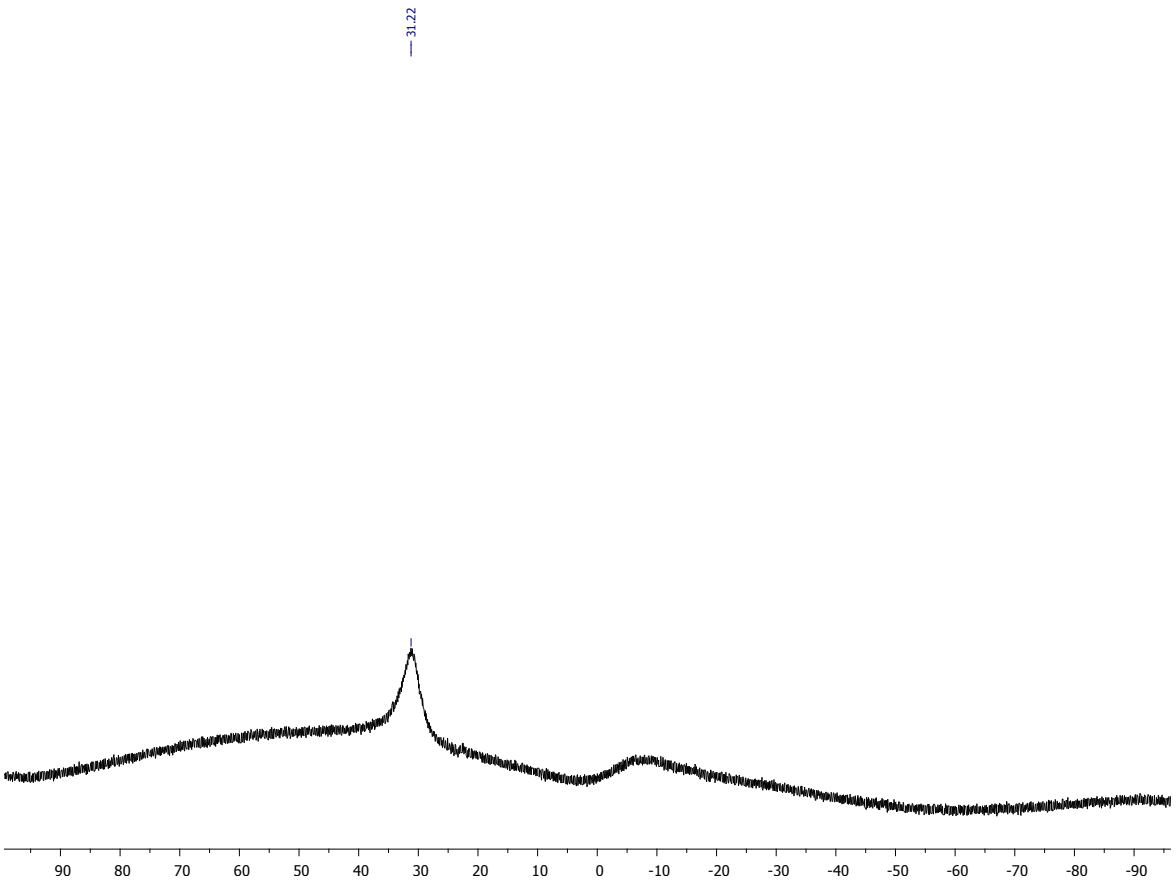
^{11}B NMR spectrum of 40



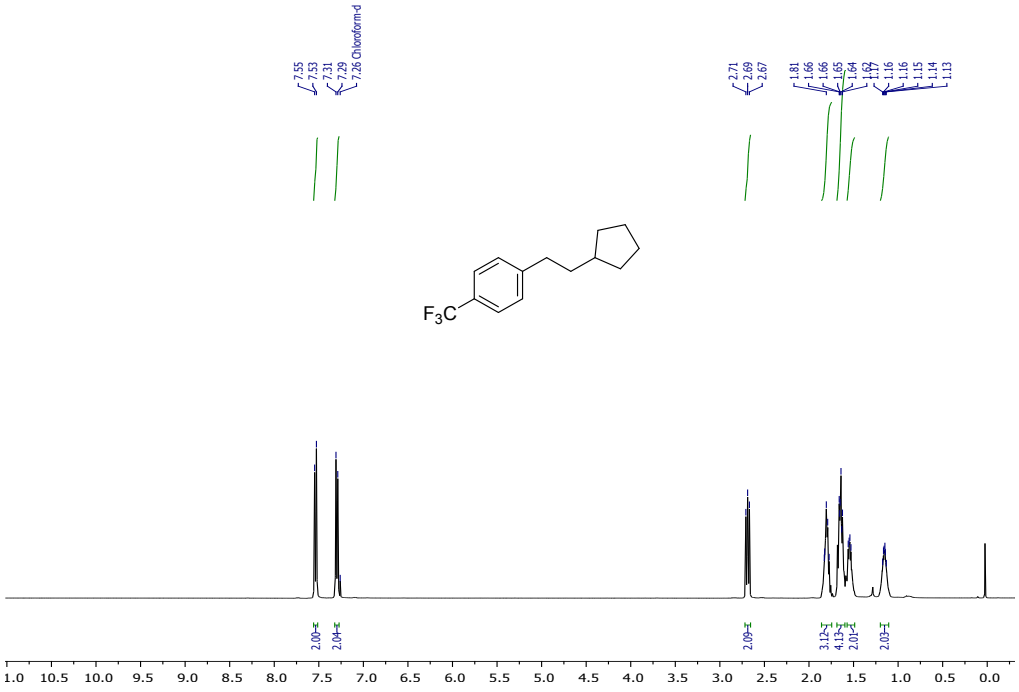
^{1}H NMR spectrum of 43



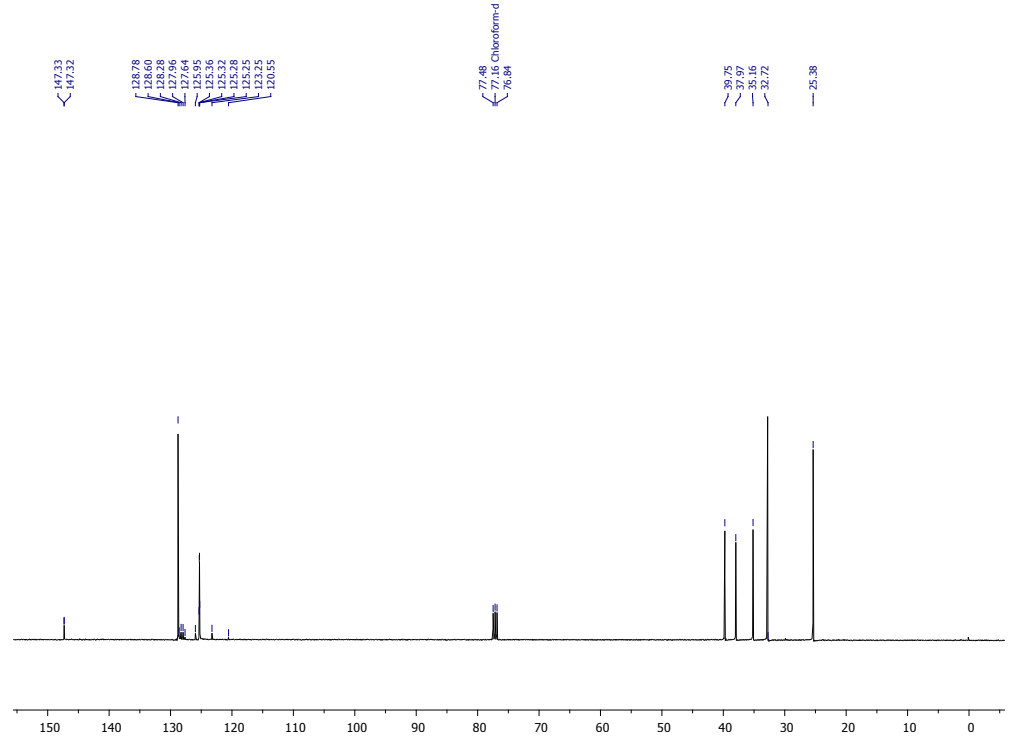
^{13}C NMR spectrum of 43



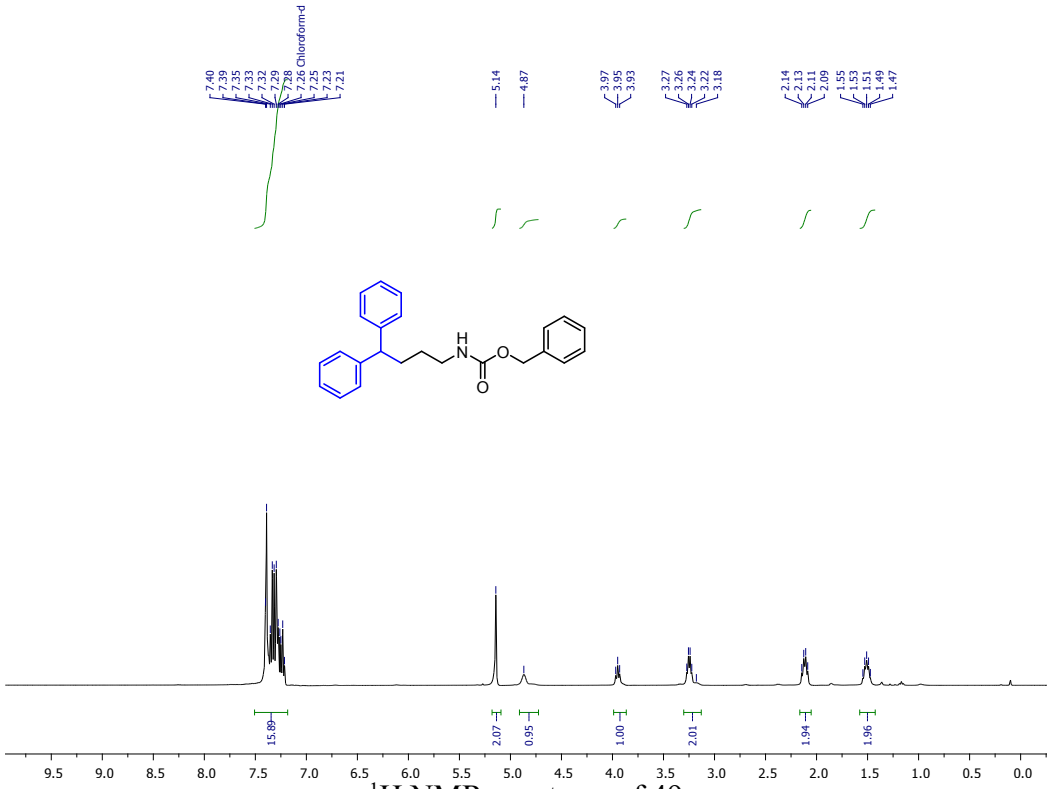
^{11}B NMR spectrum of 43



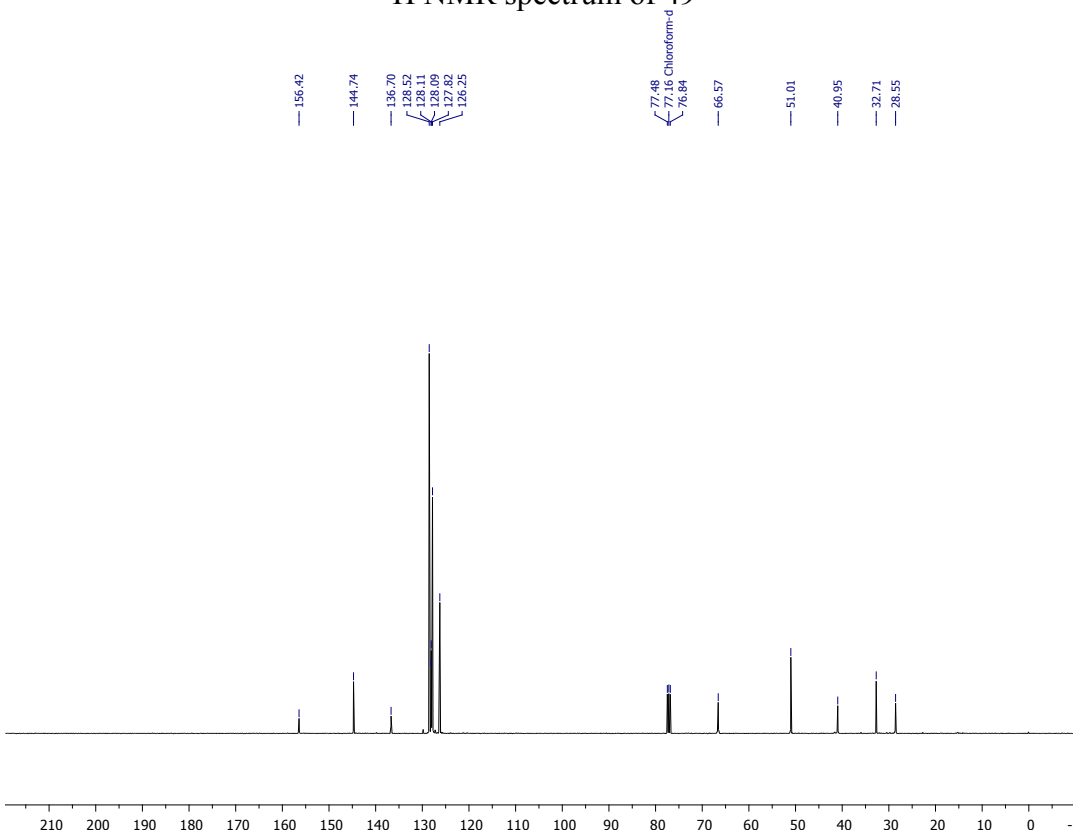
^{1}H NMR spectrum of 46



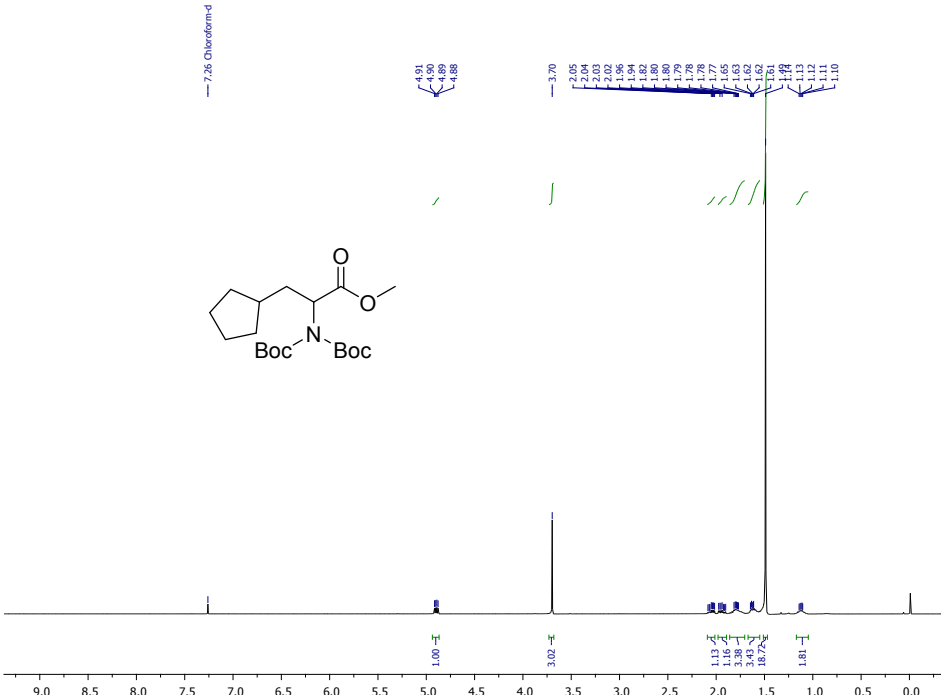
^{13}C NMR spectrum of 46



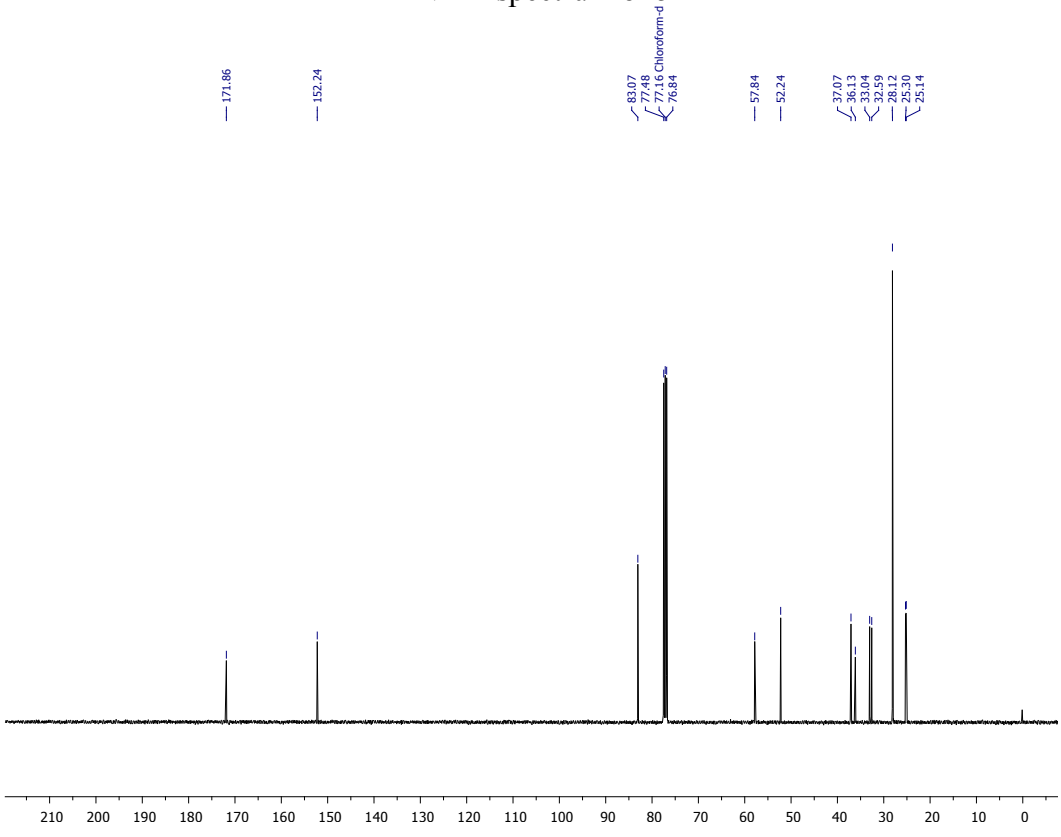
^{1}H NMR spectrum of 49



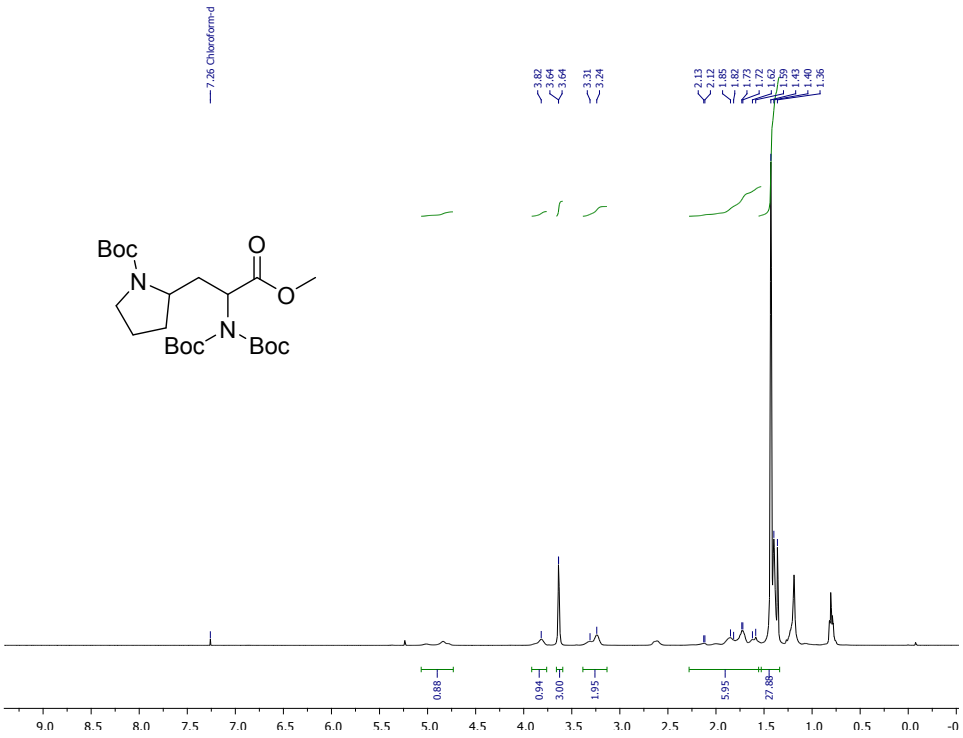
^{13}C NMR spectrum of 49



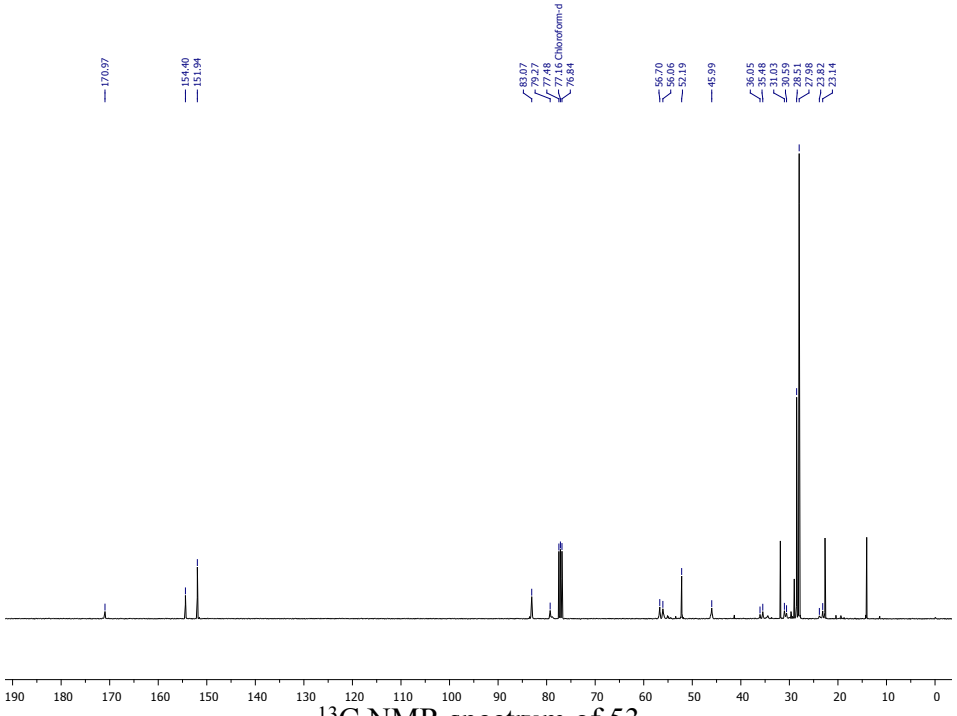
^{1}H NMR spectrum of 51



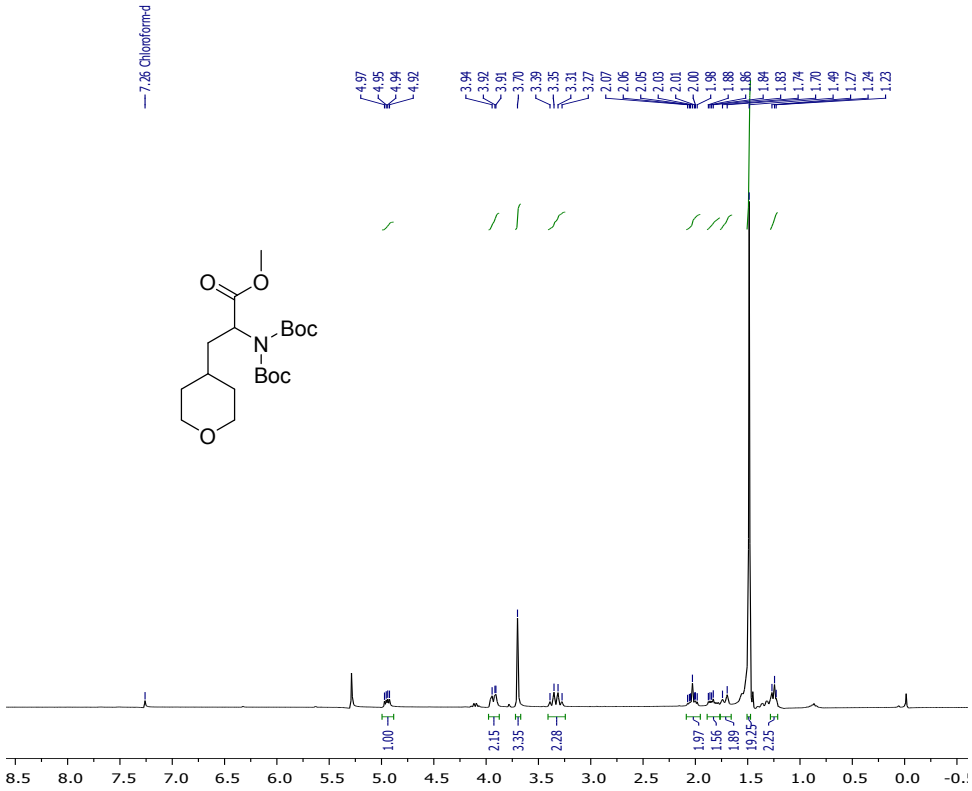
^{13}C NMR spectrum of 51



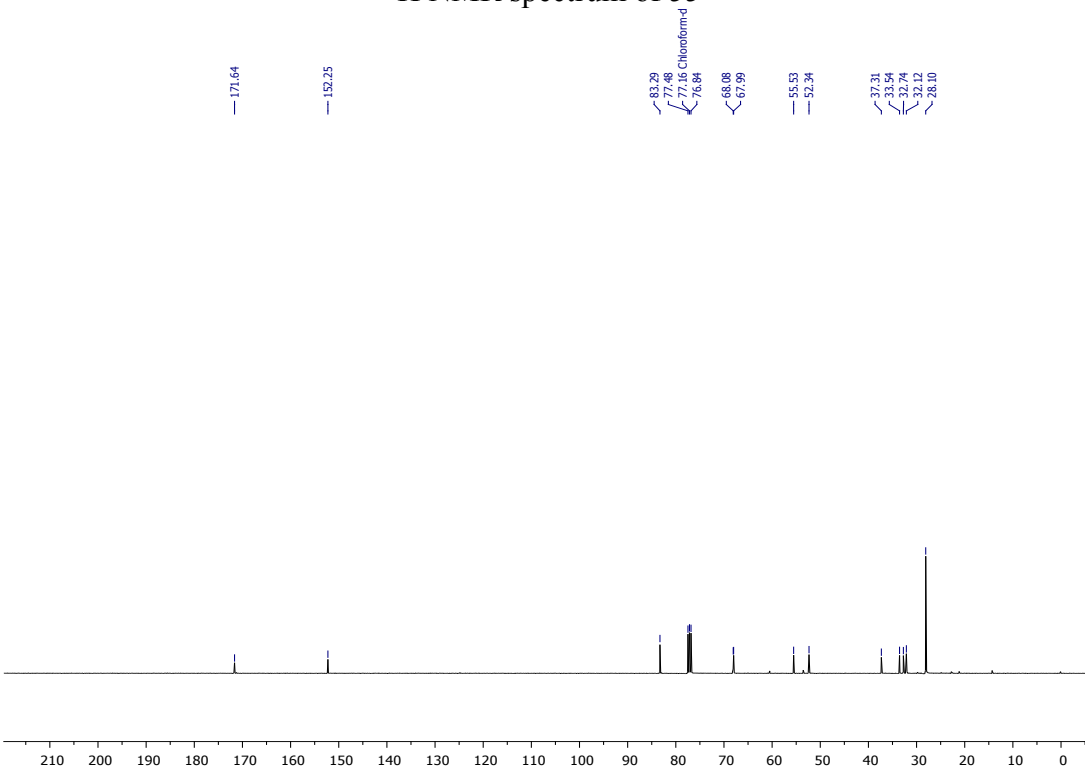
^{1}H NMR spectrum of 53



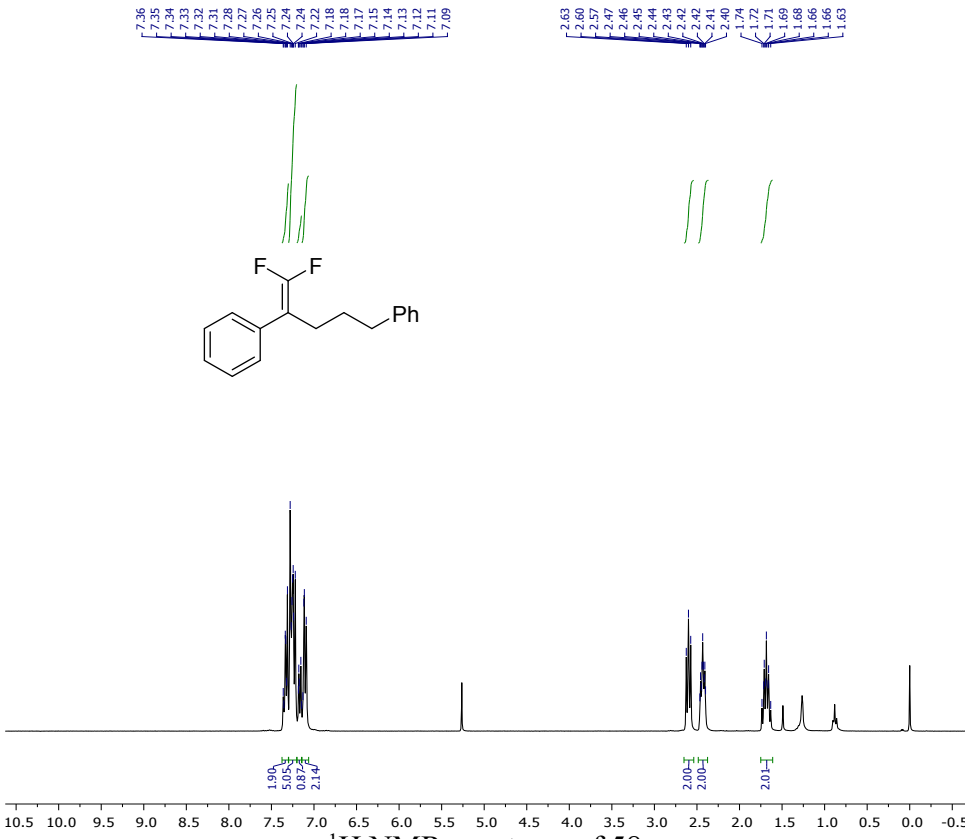
^{13}C NMR spectrum of 53



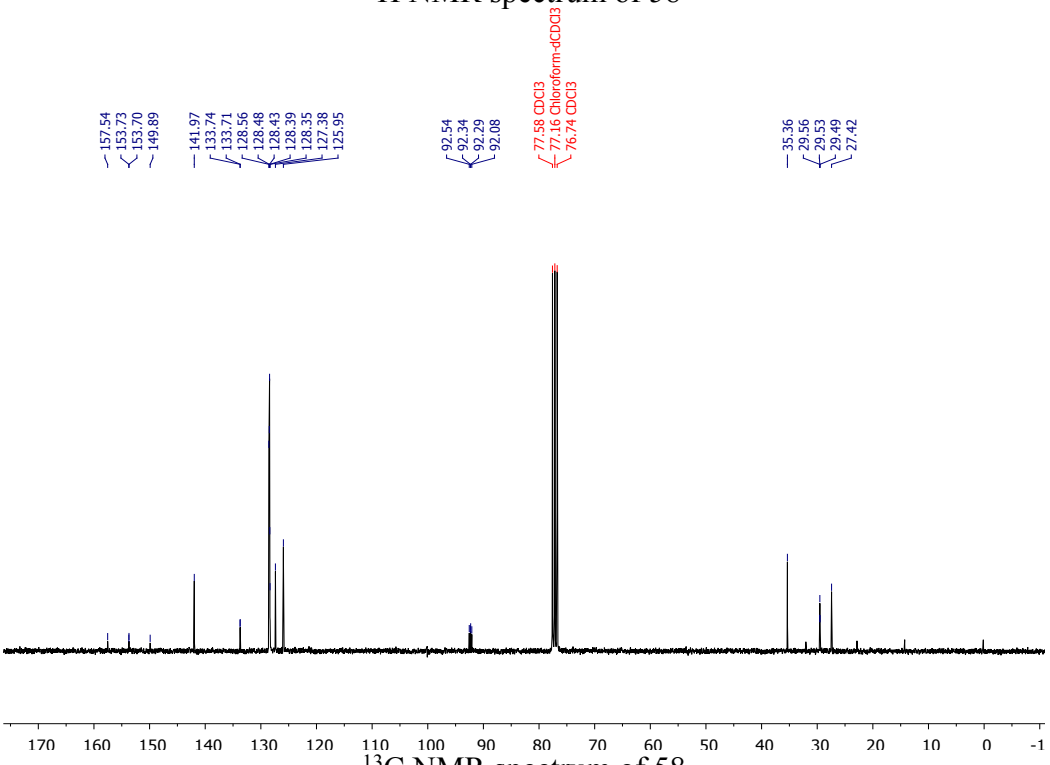
^{1}H NMR spectrum of 55



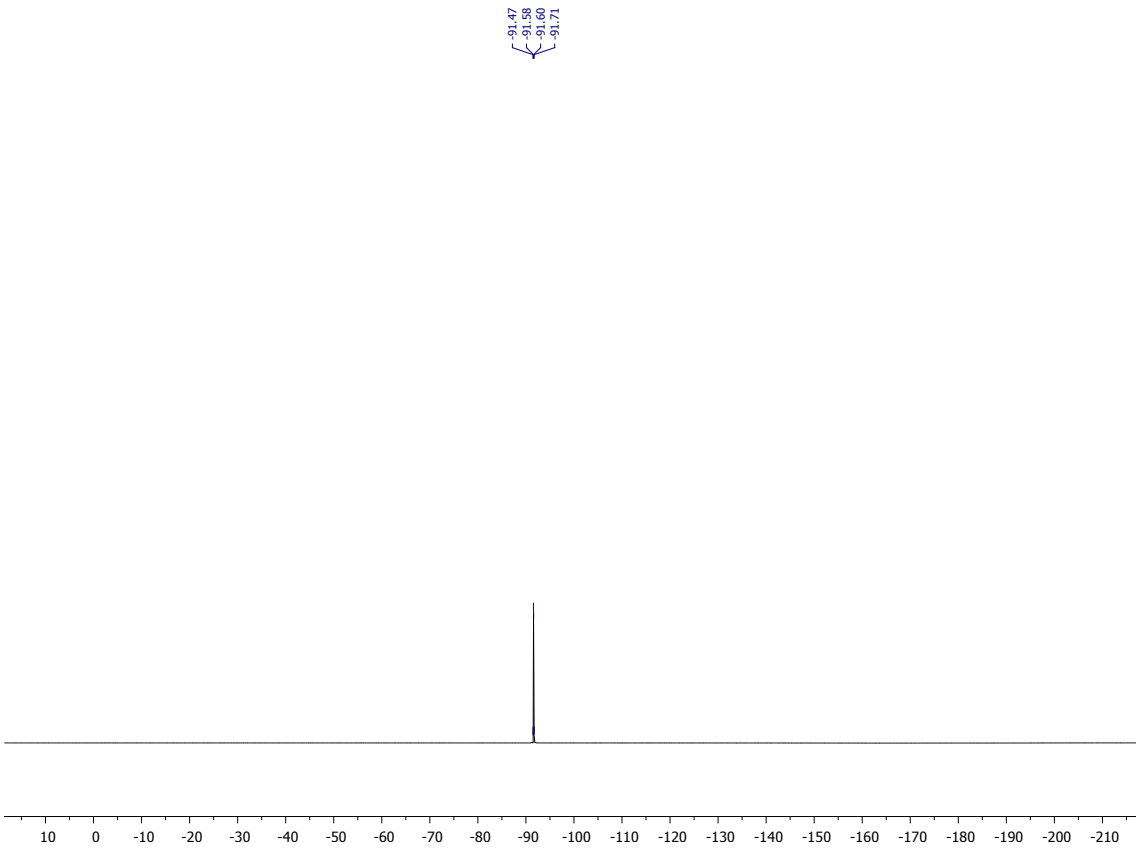
^{13}C NMR spectrum of 55



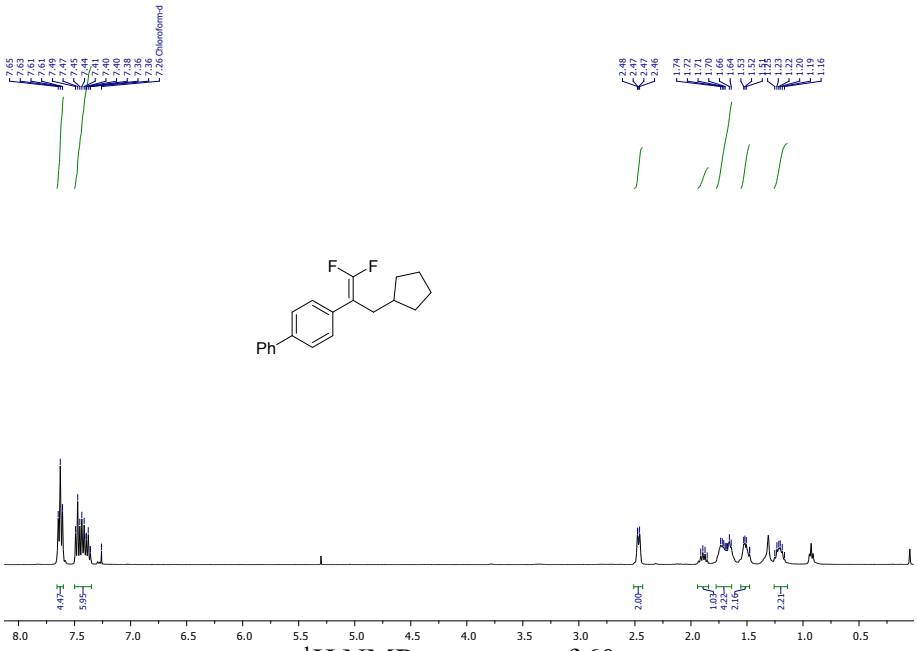
^{1}H NMR spectrum of 58



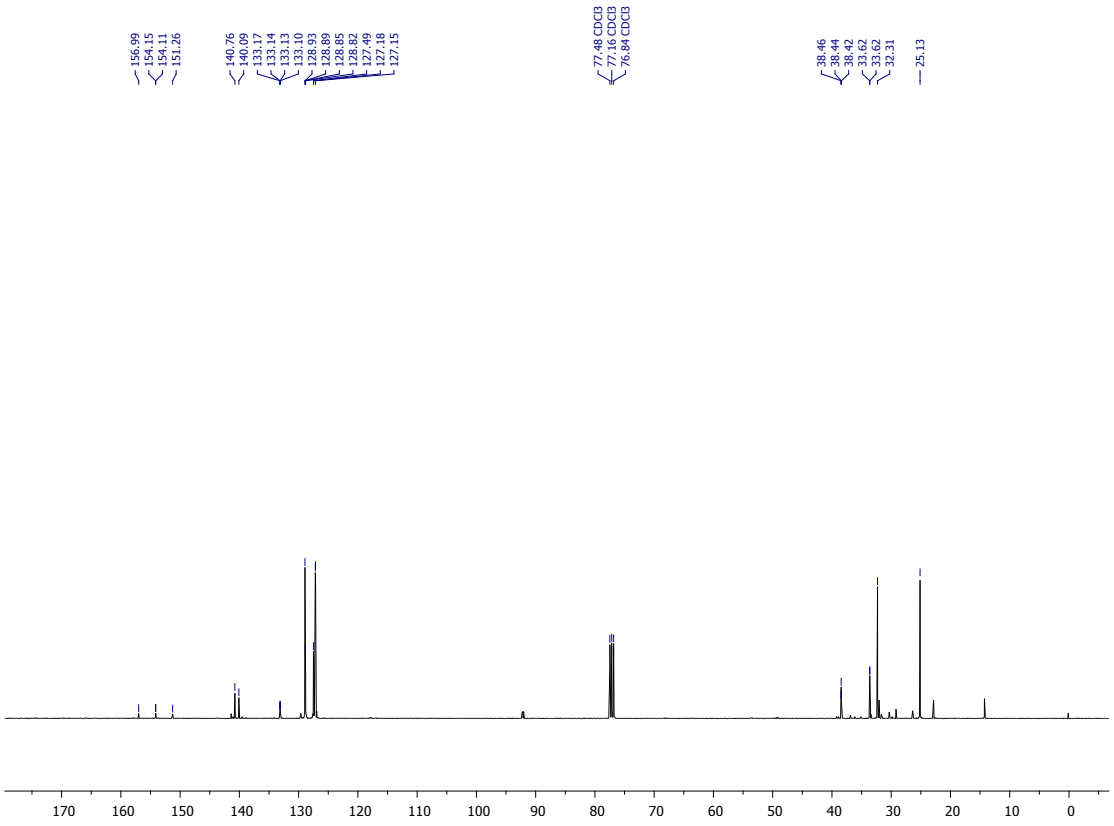
^{13}C NMR spectrum of 58



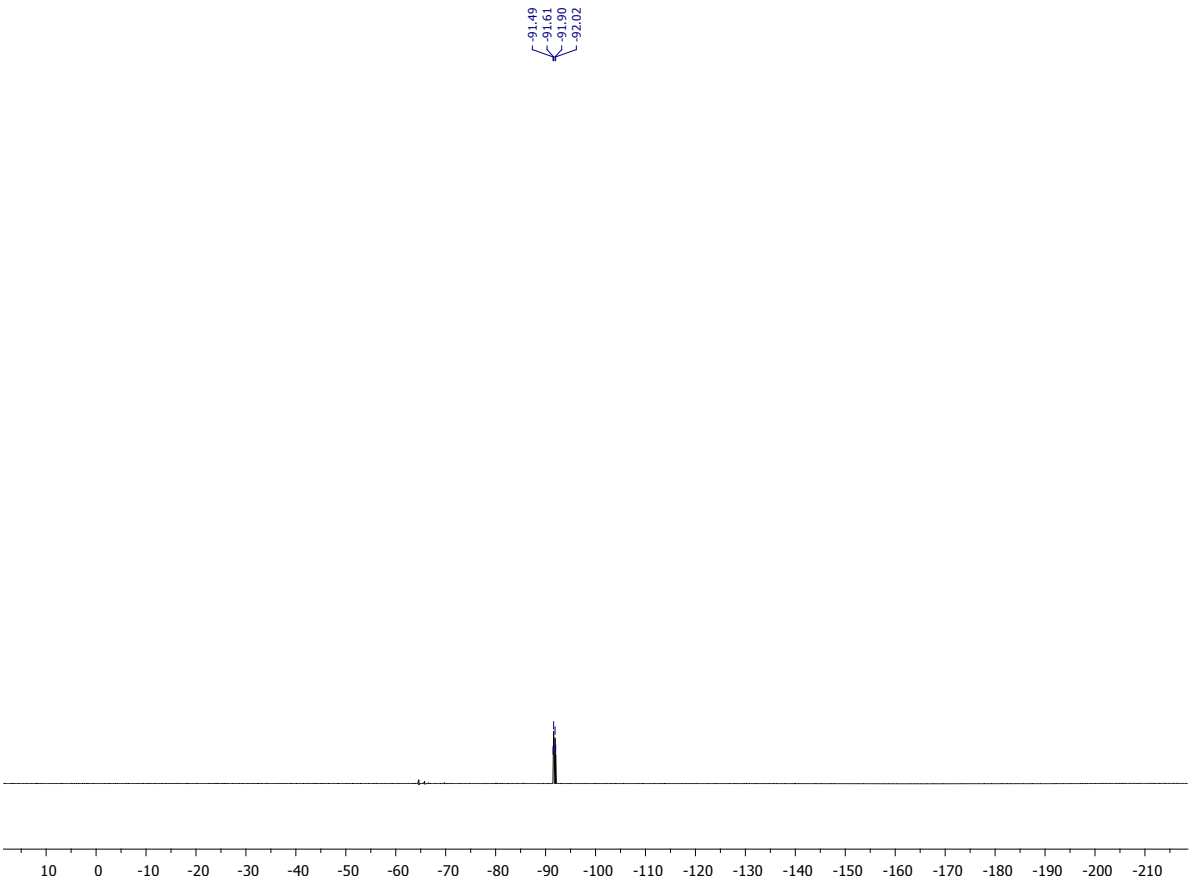
^{19}F NMR spectrum 58



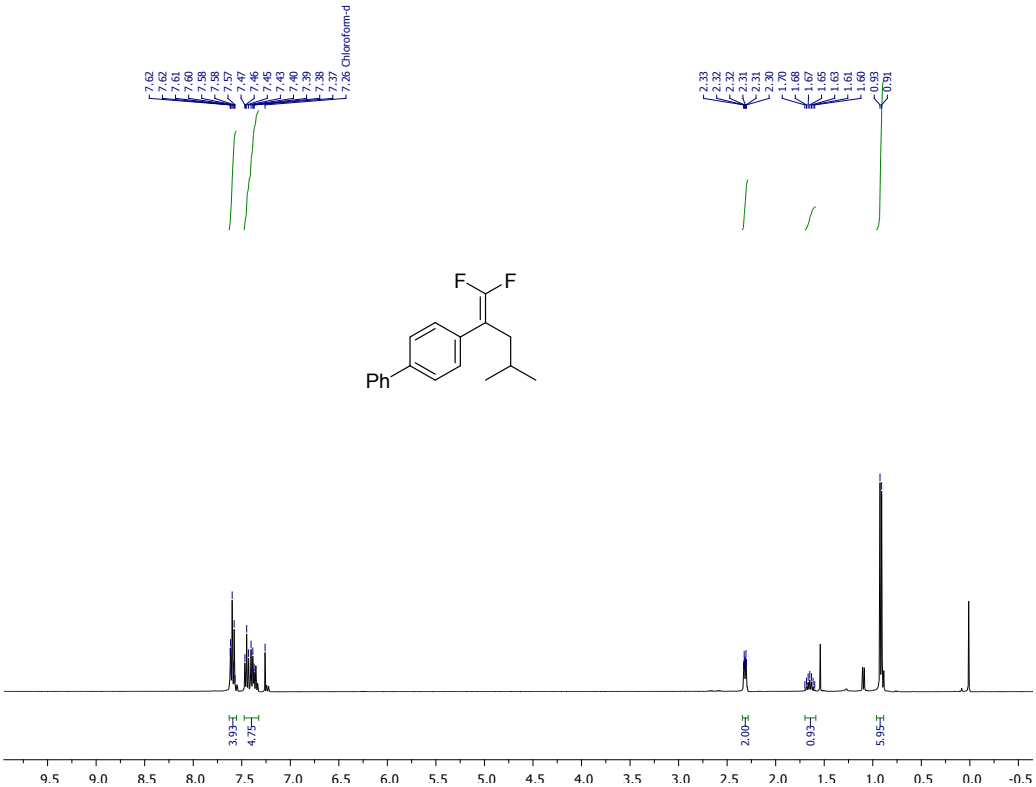
^{1}H NMR spectrum of 60



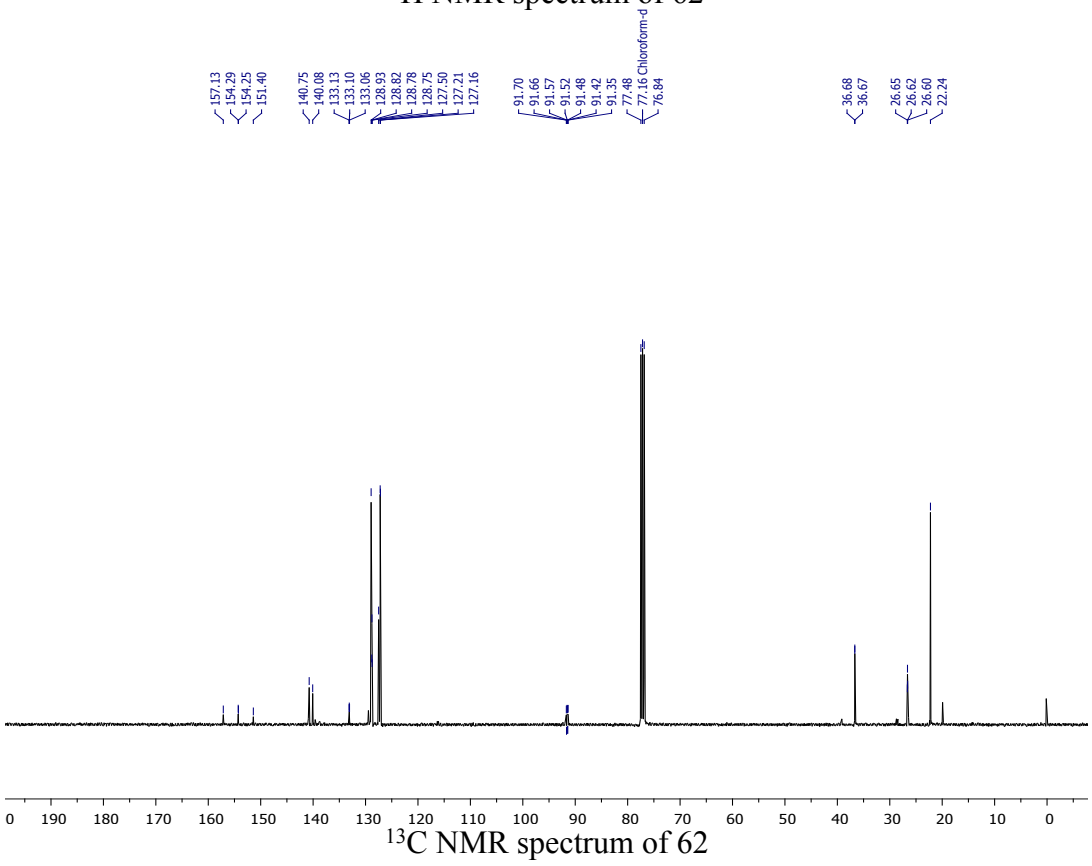
^{13}C NMR spectrum of 60



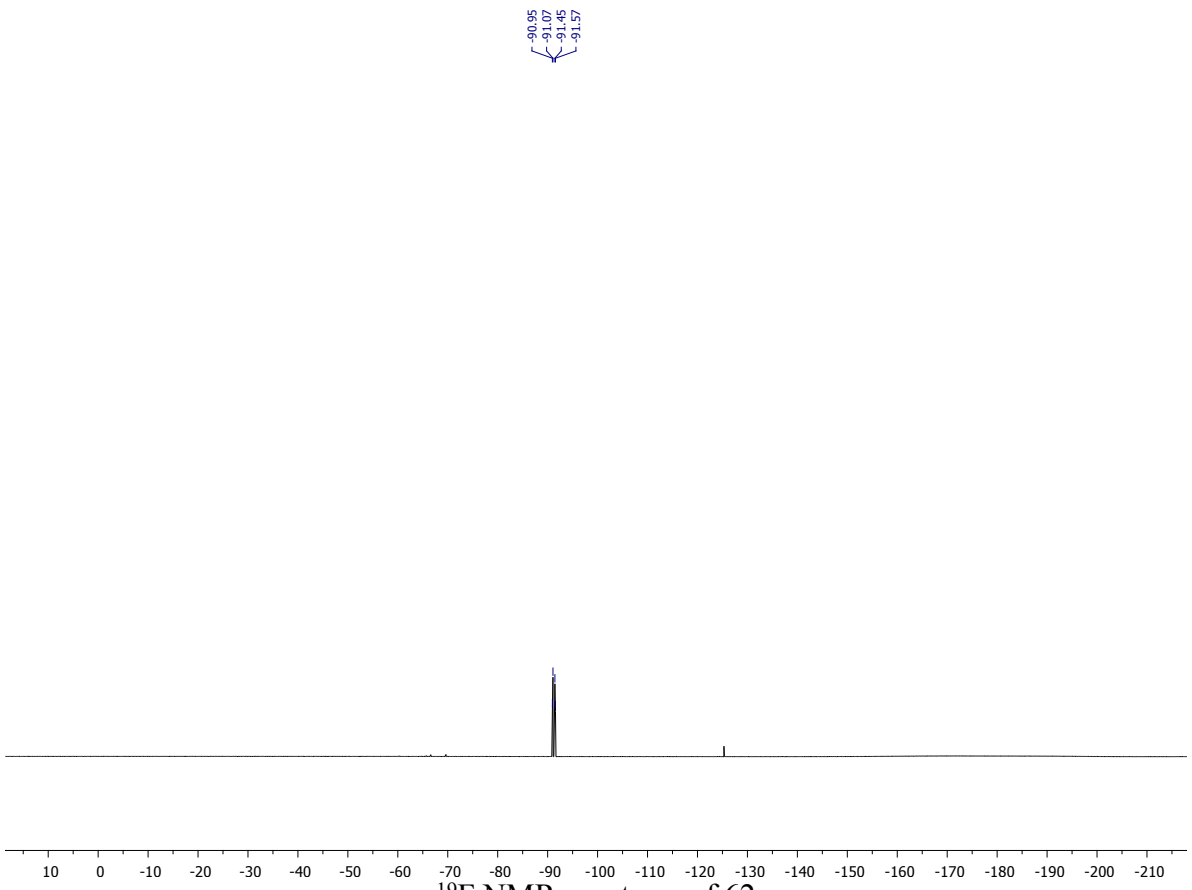
^{19}F NMR spectrum of 60



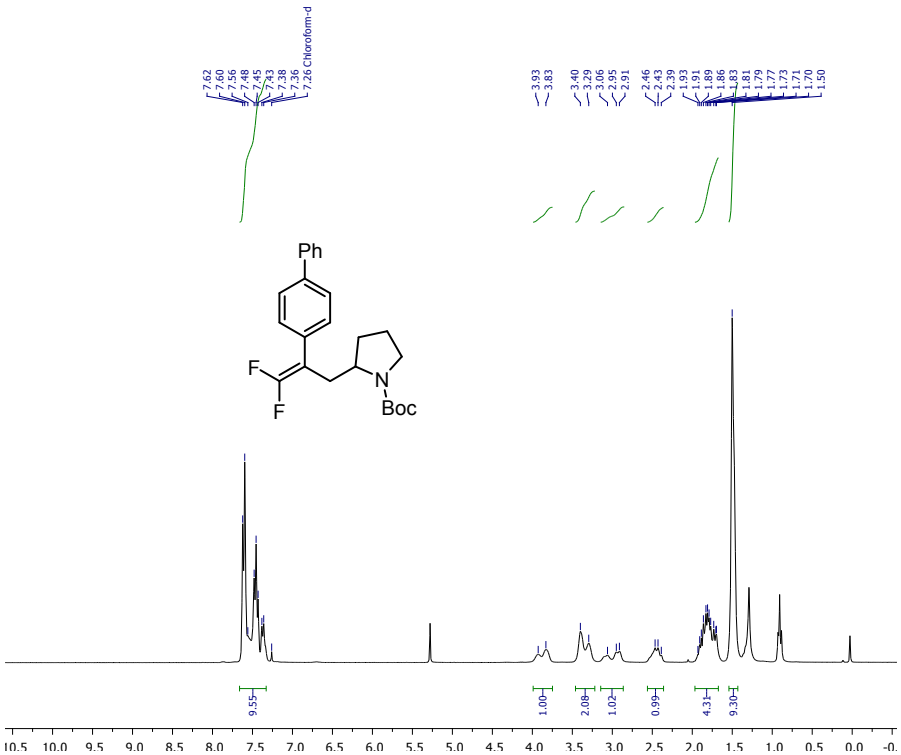
^{1}H NMR spectrum of 62



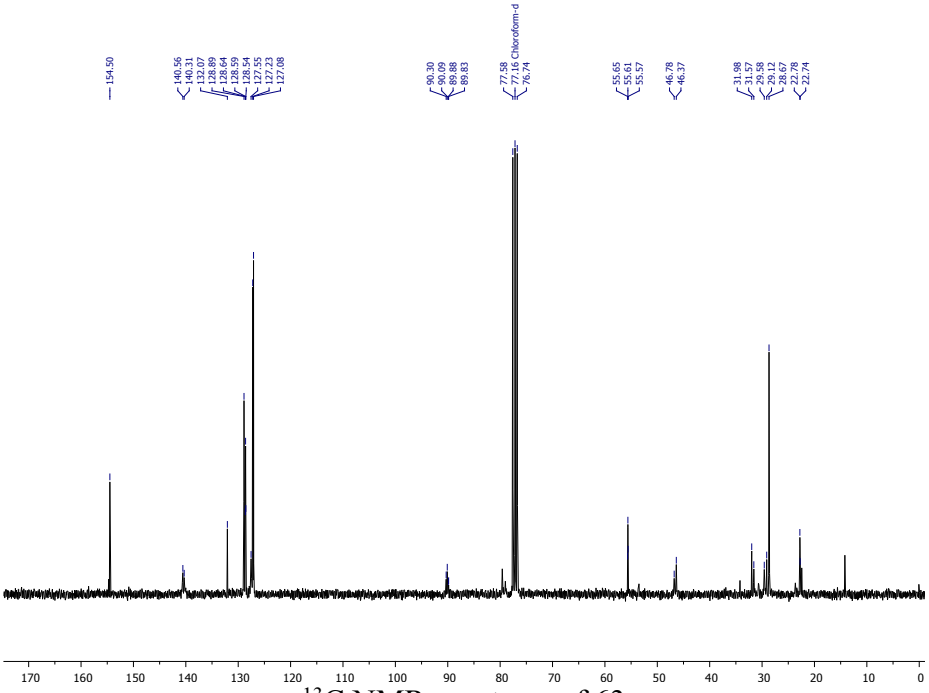
^{13}C NMR spectrum of 62



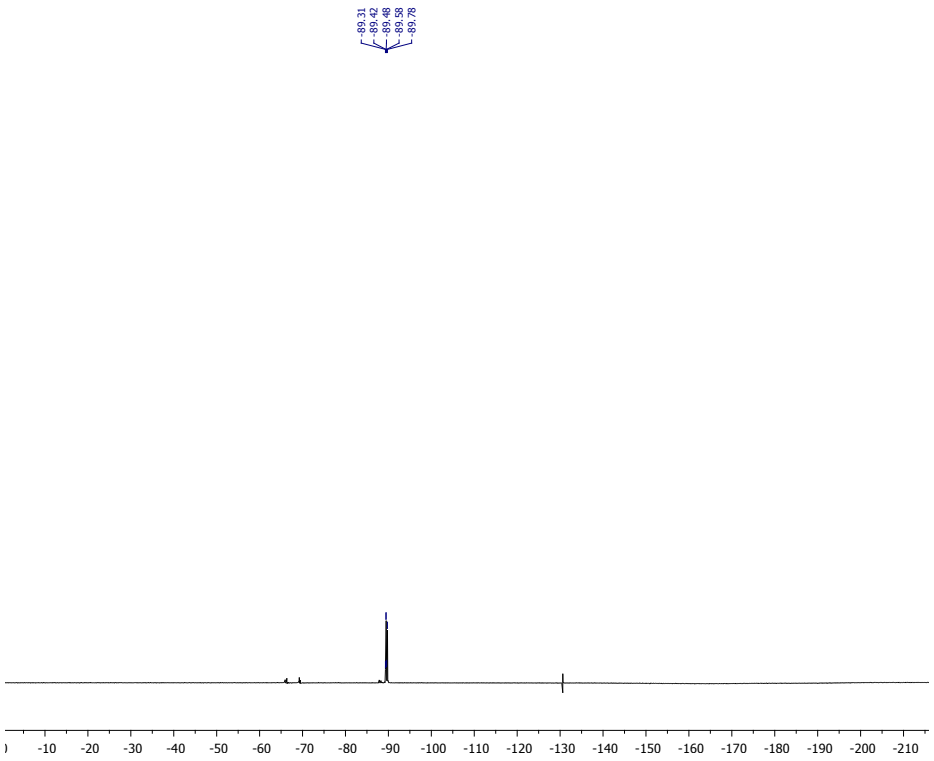
^{19}F NMR spectrum of 62



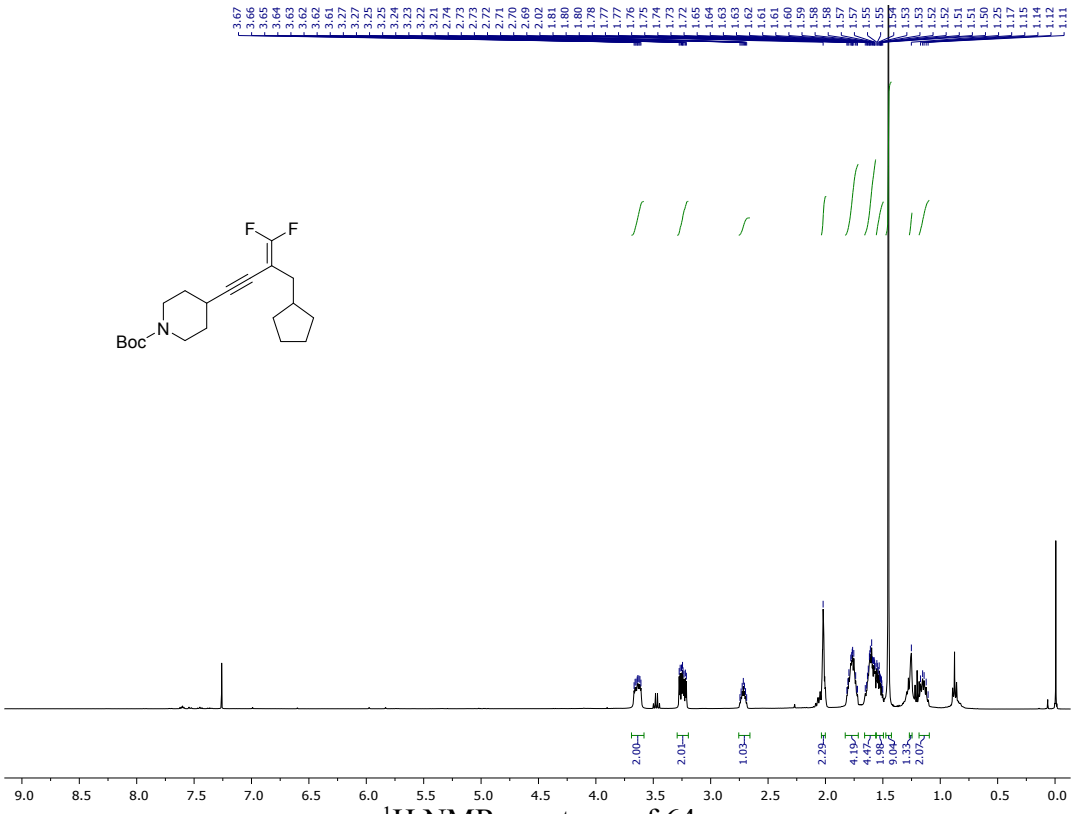
^{1}H NMR spectrum of 63



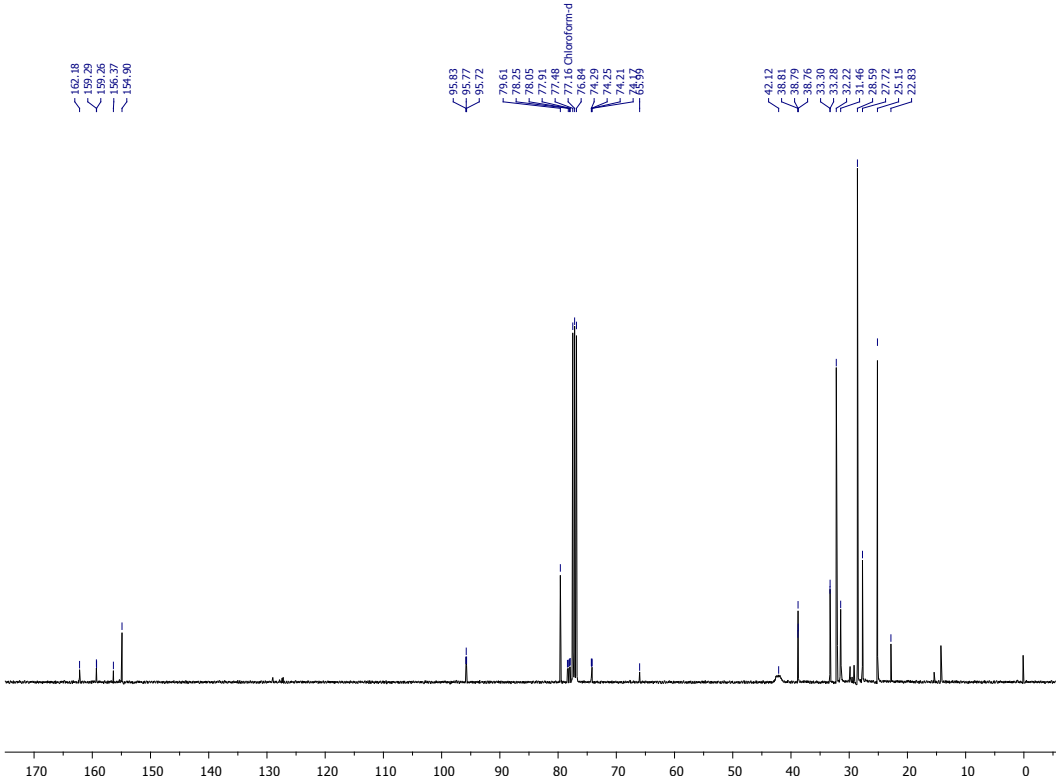
^{13}C NMR spectrum of 63



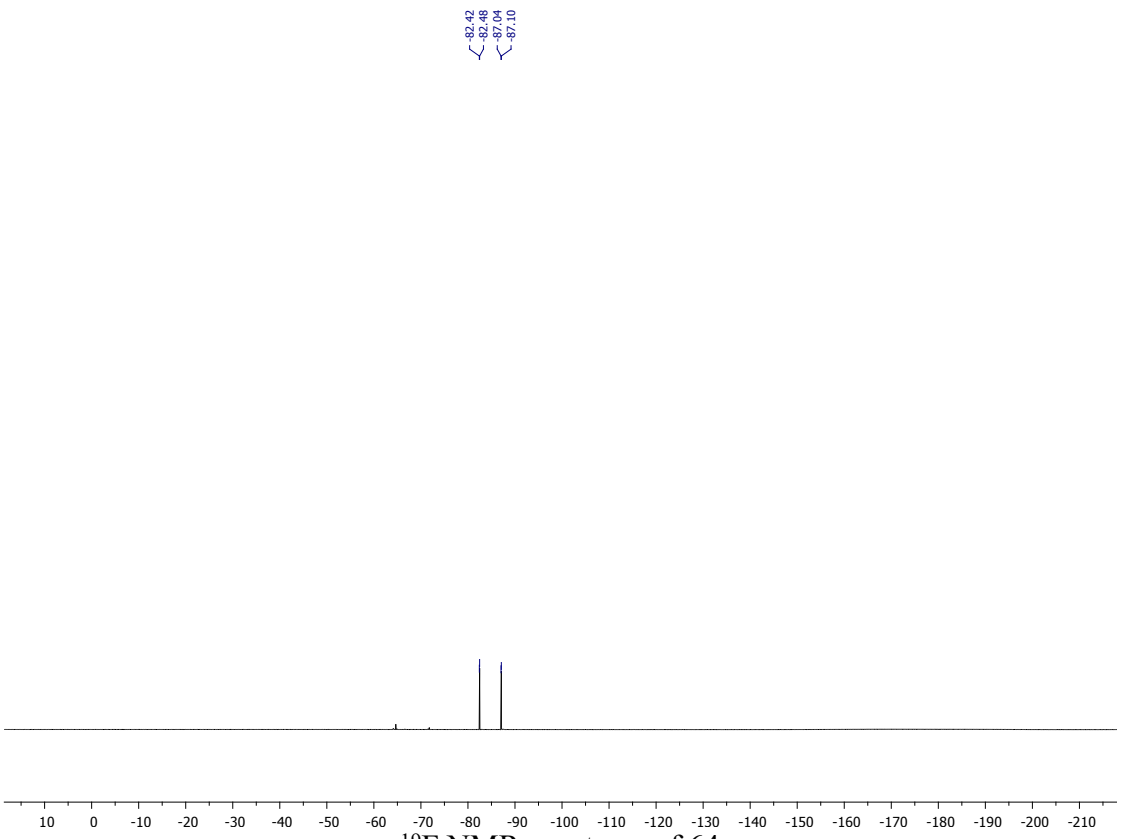
^{19}F NMR spectrum of 63



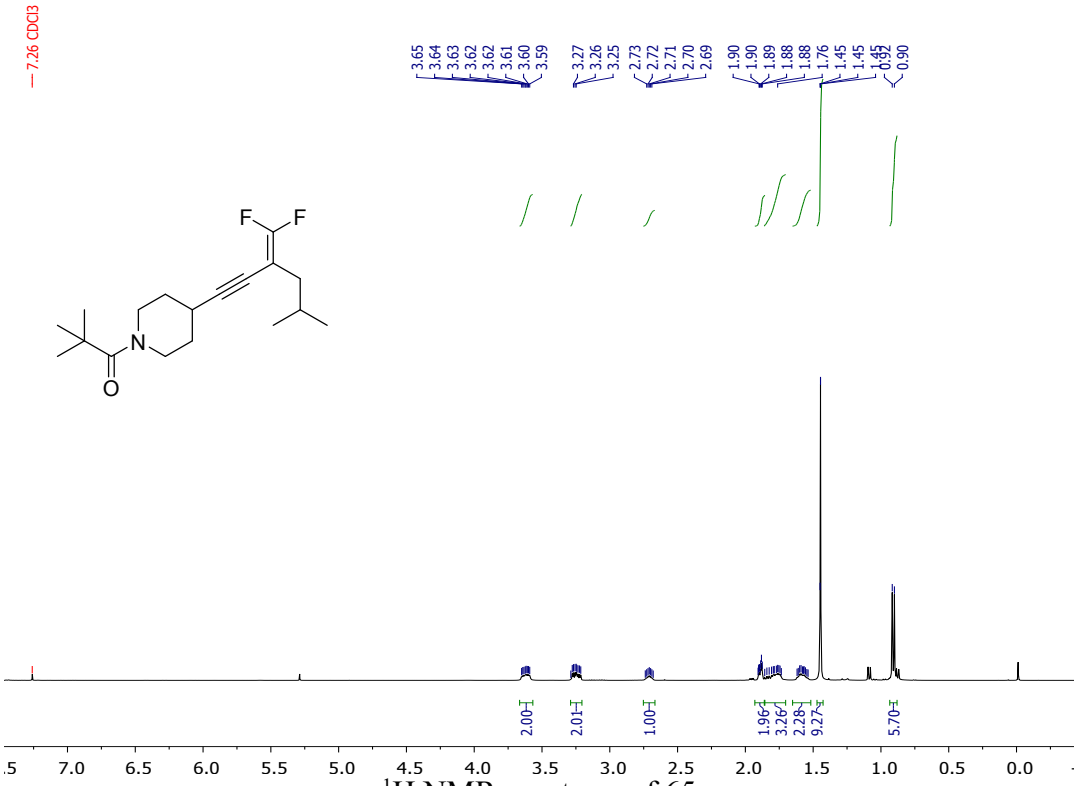
^{1}H NMR spectrum of 64



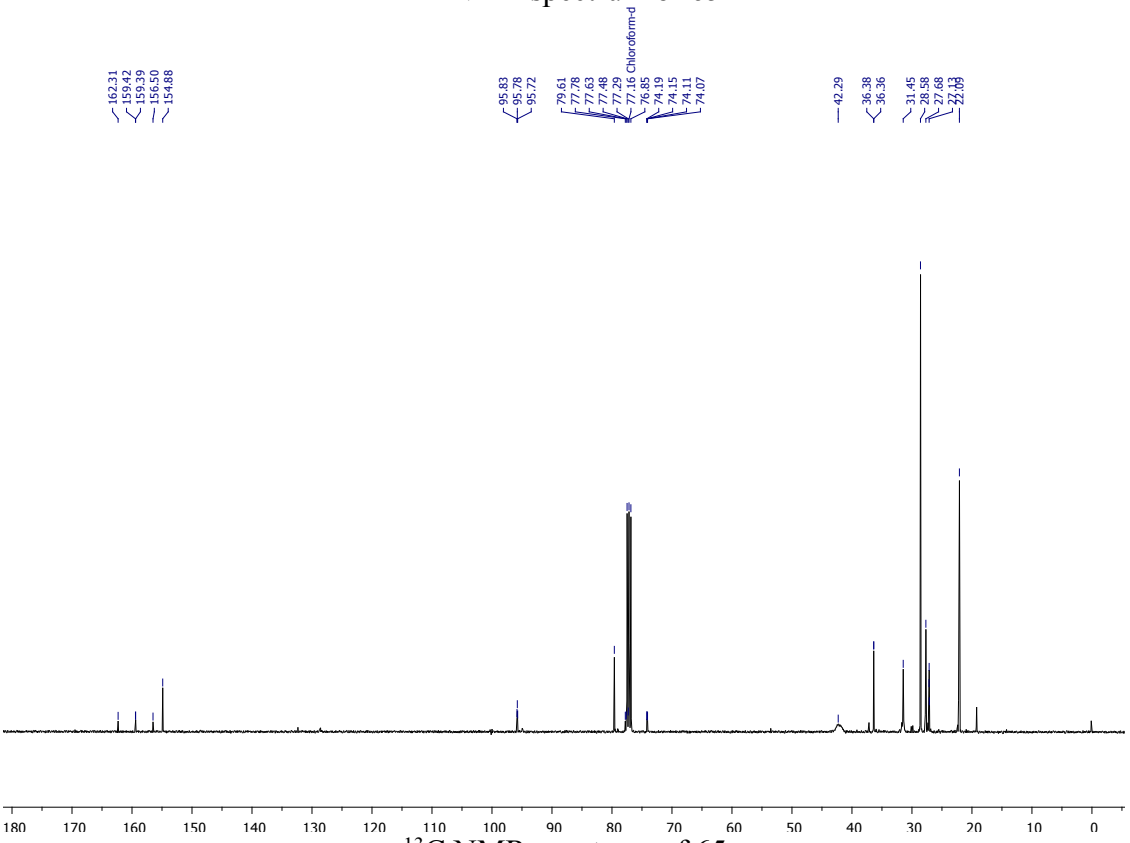
^{13}C NMR spectrum of 64



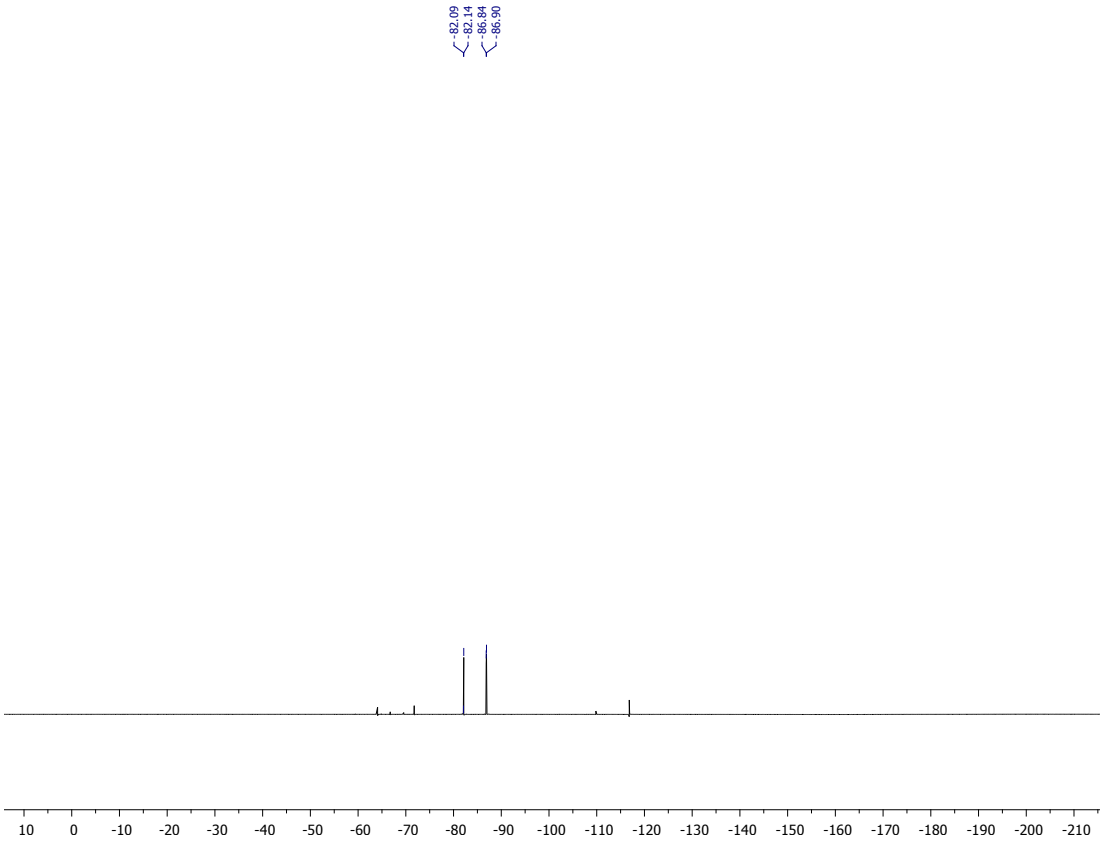
^{19}F NMR spectrum of 64



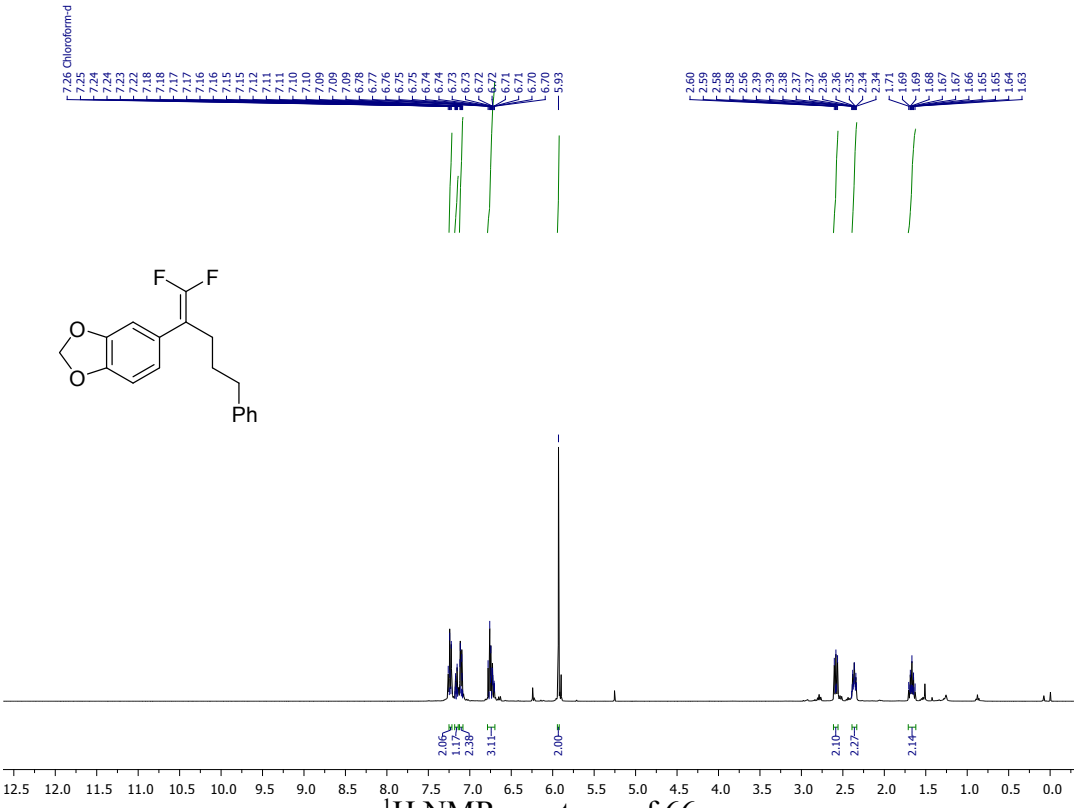
^{1}H NMR spectrum of 65



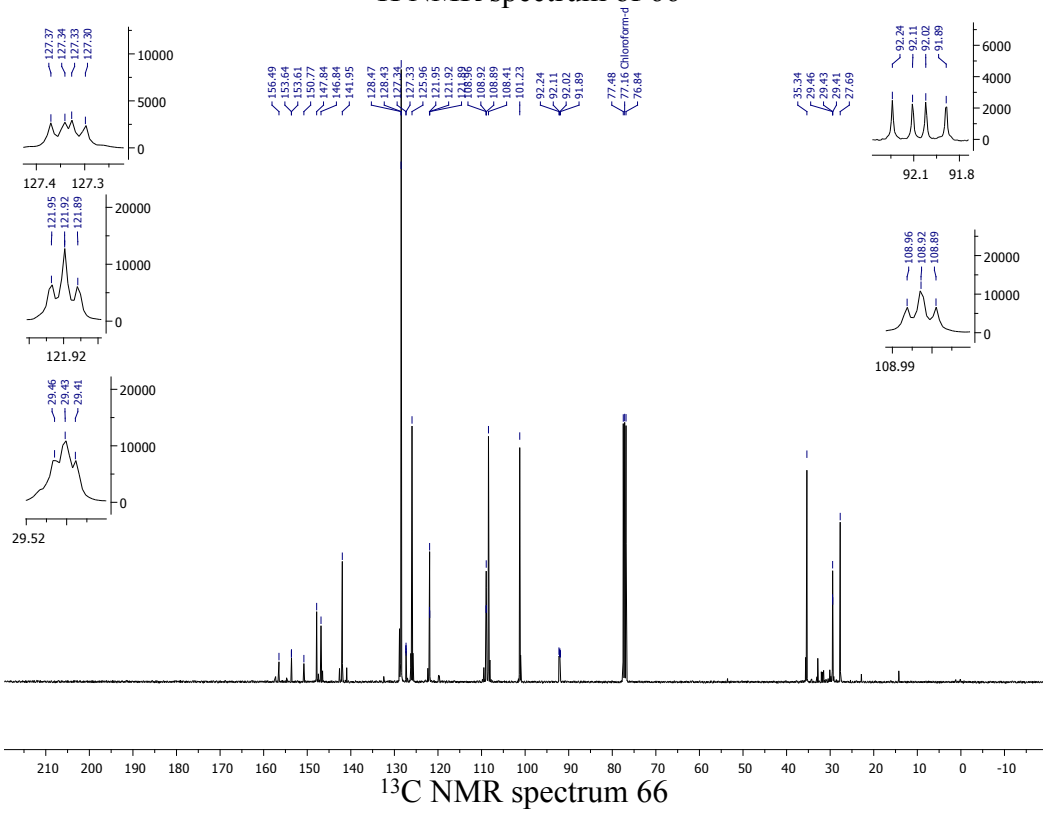
^{13}C NMR spectrum of 65



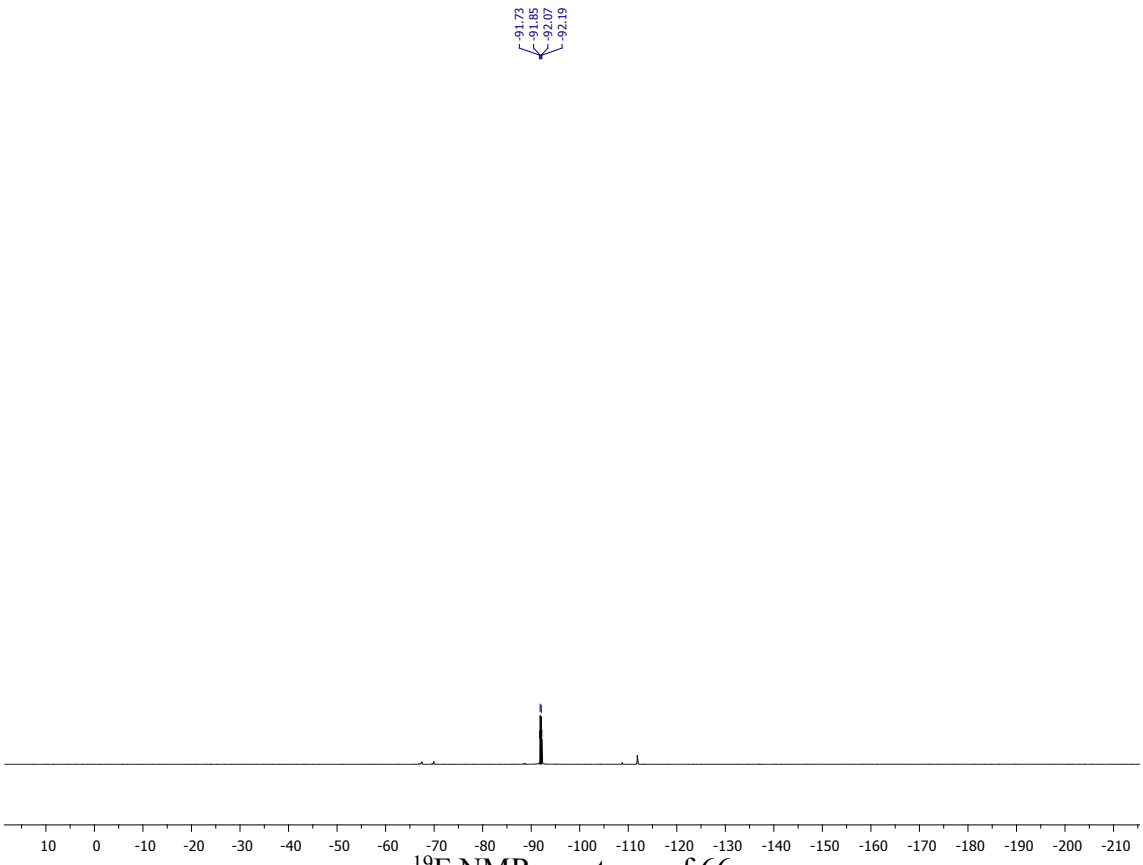
^{19}F NMR spectrum of 65



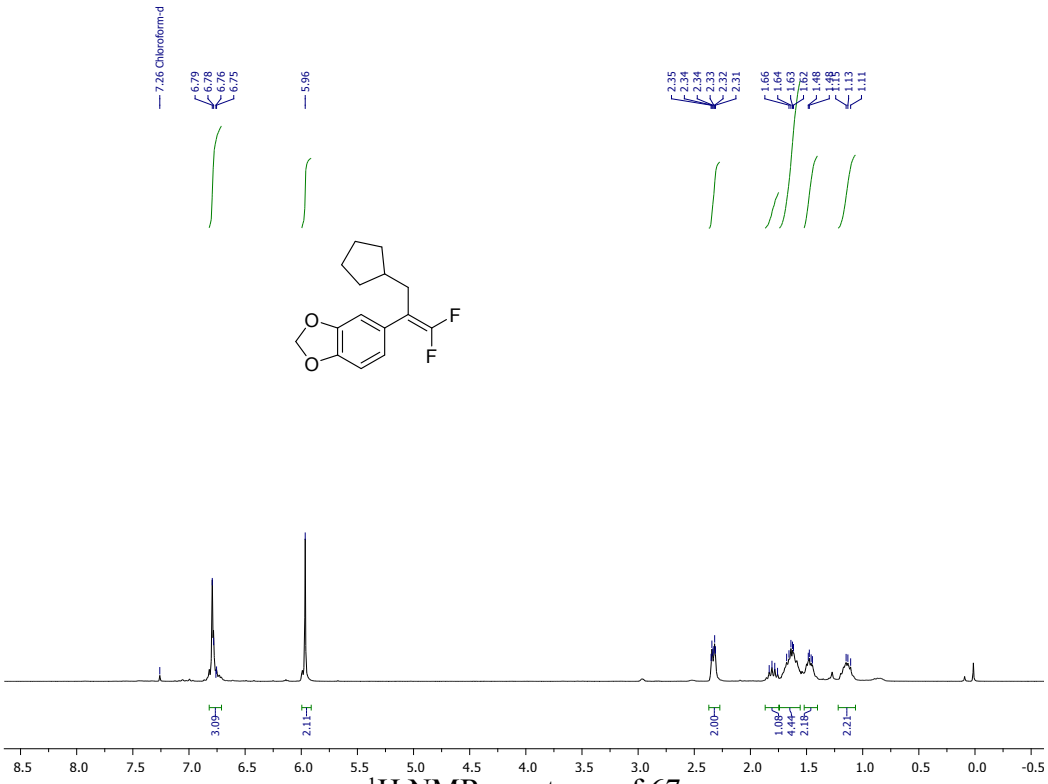
^{1}H NMR spectrum of 66



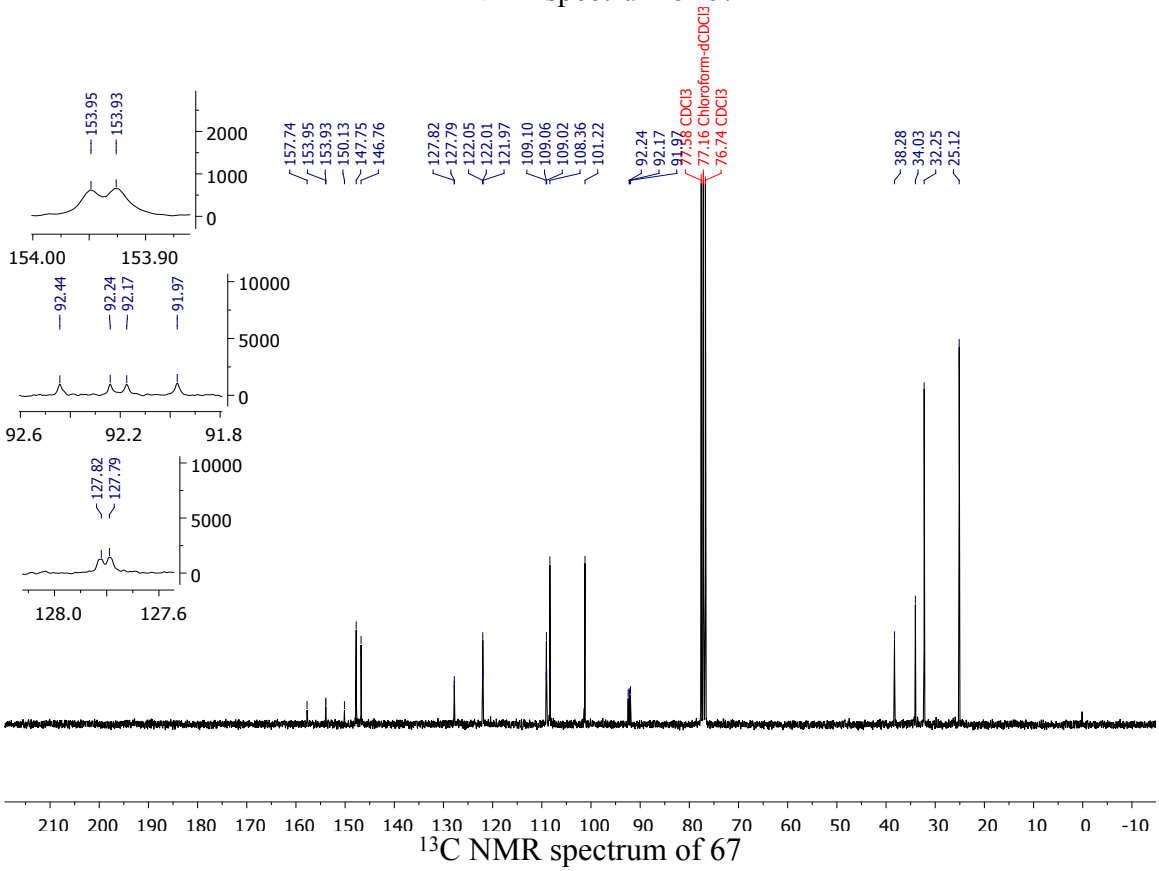
^{13}C NMR spectrum 66



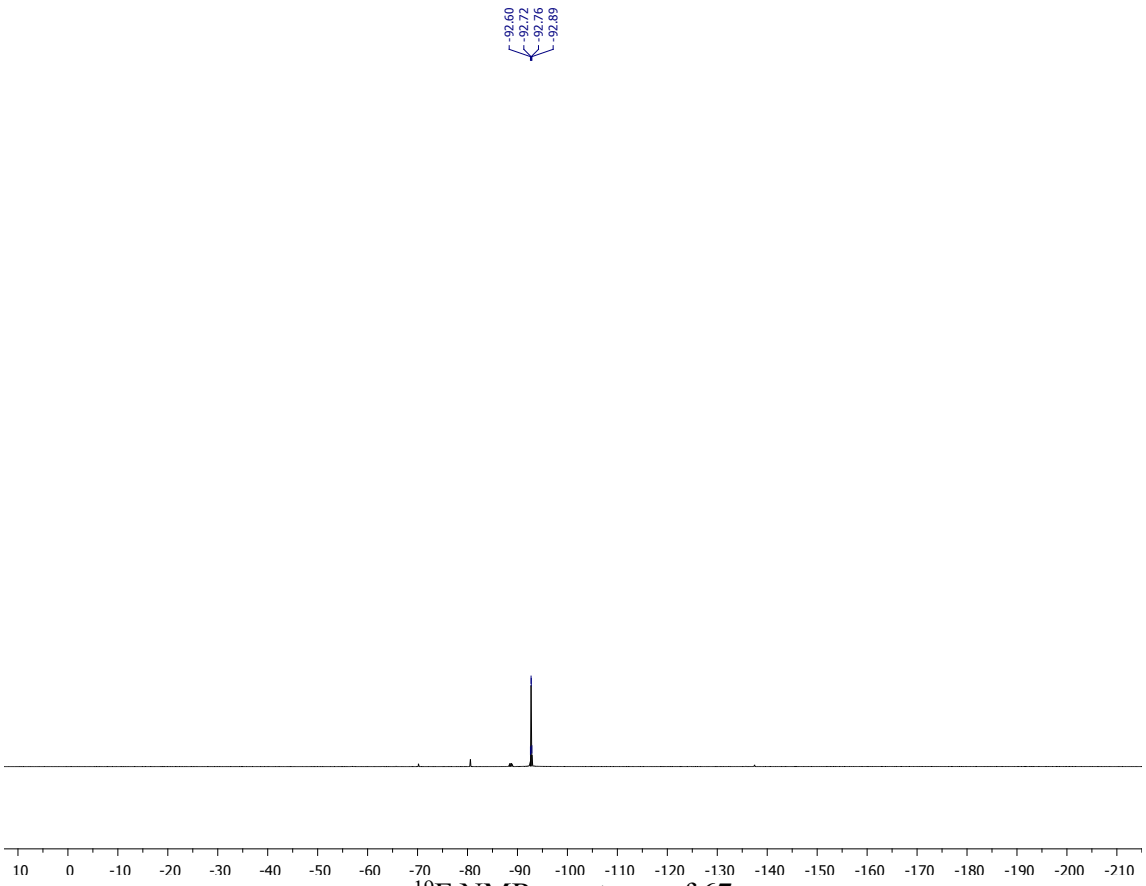
^{19}F NMR spectrum of 66



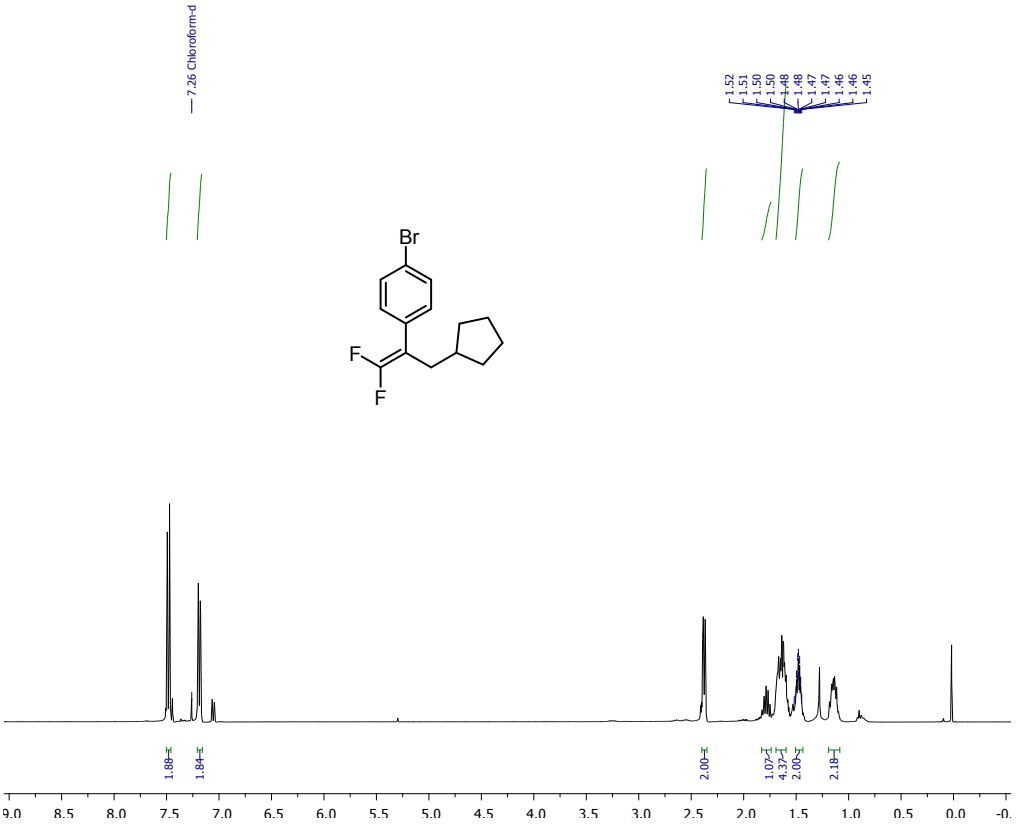
^{1}H NMR spectrum of 67



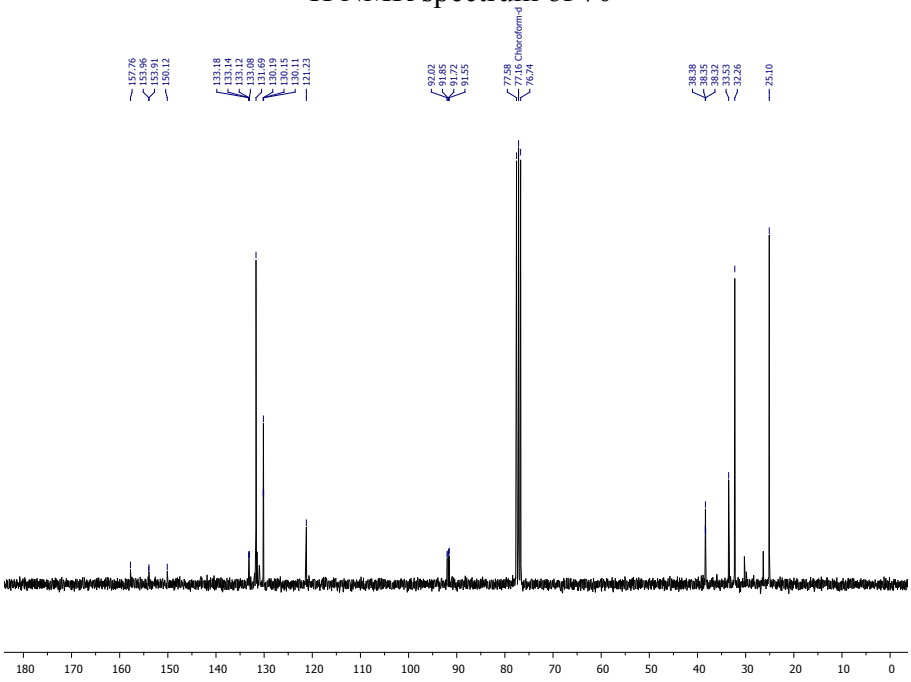
^{13}C NMR spectrum of 67



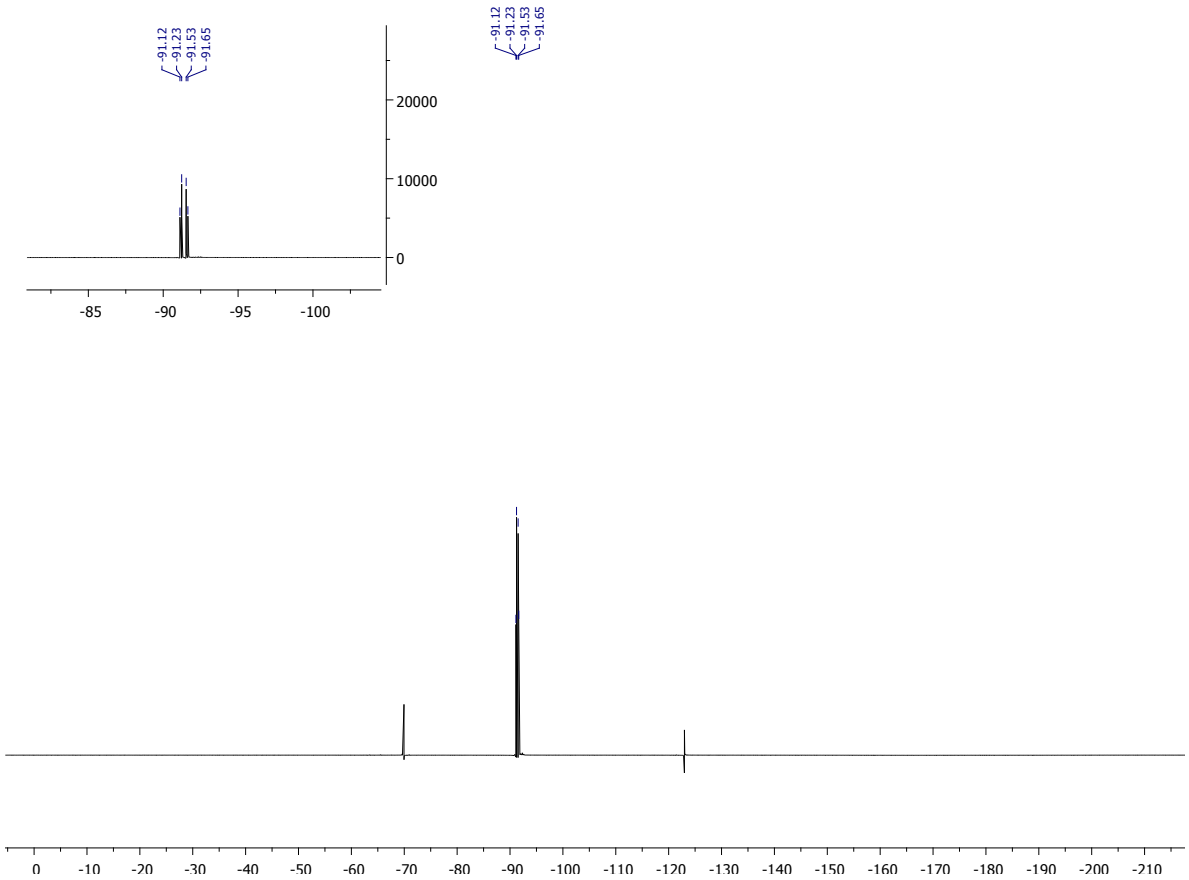
^{19}F NMR spectrum of 67



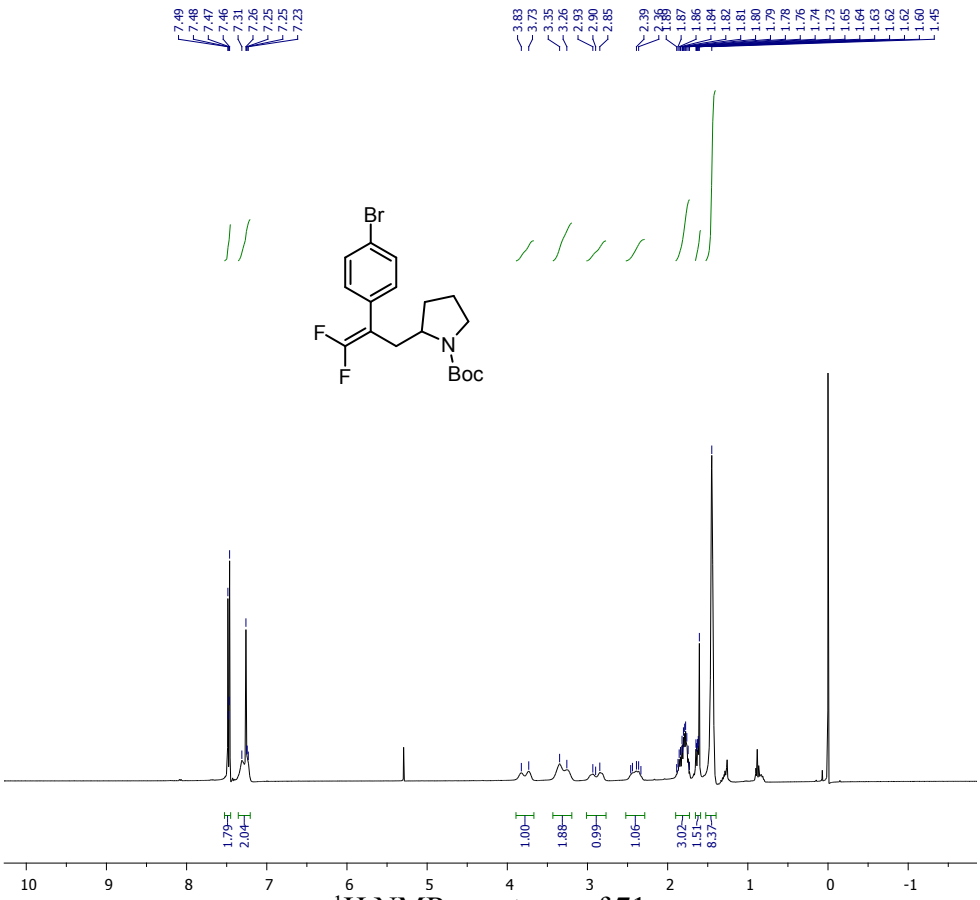
^{1}H NMR spectrum of 70



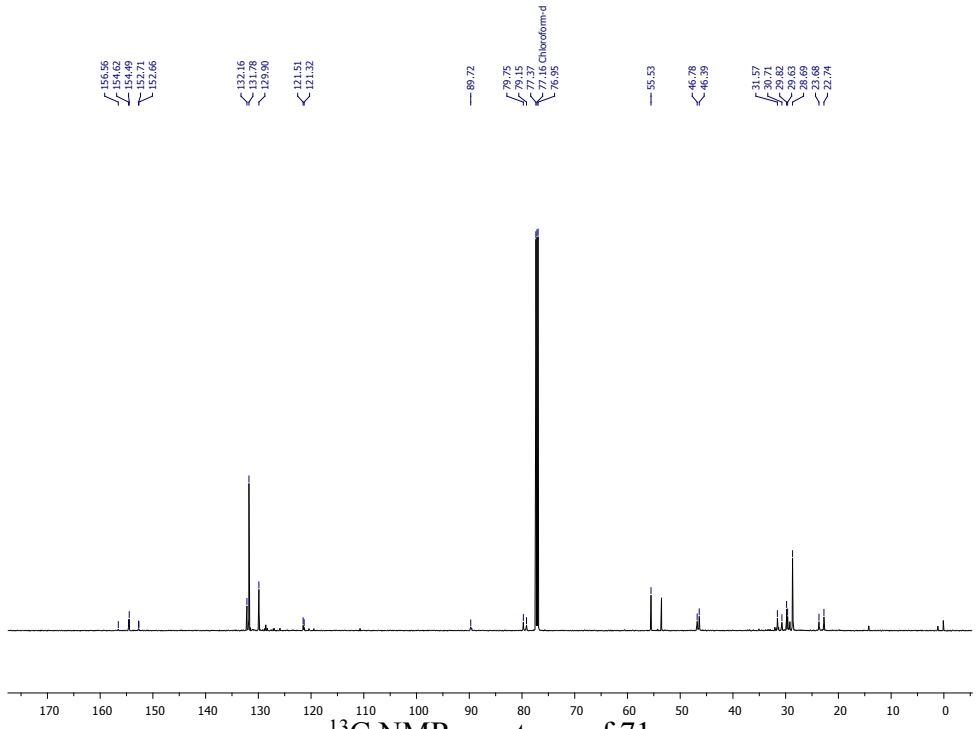
^{13}C NMR spectrum of 70



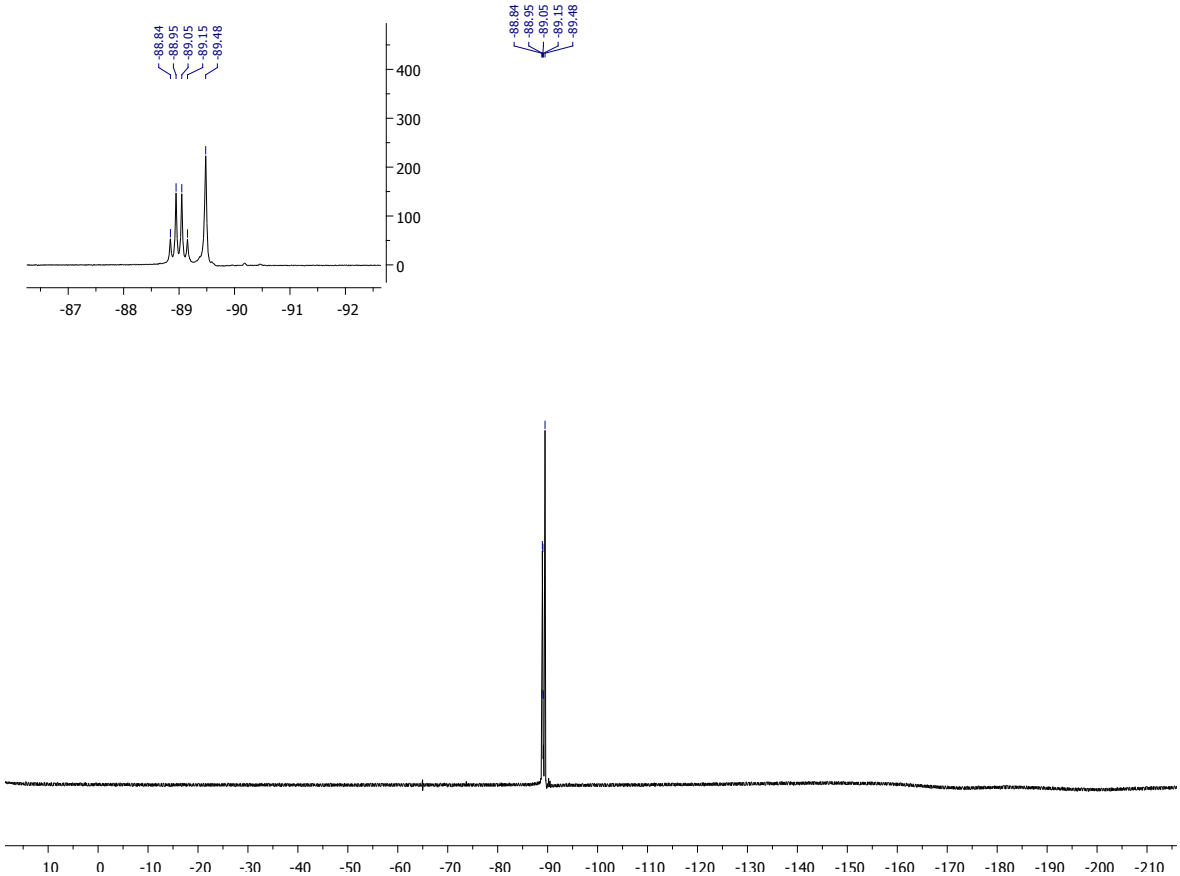
^{19}F NMR spectrum of 70



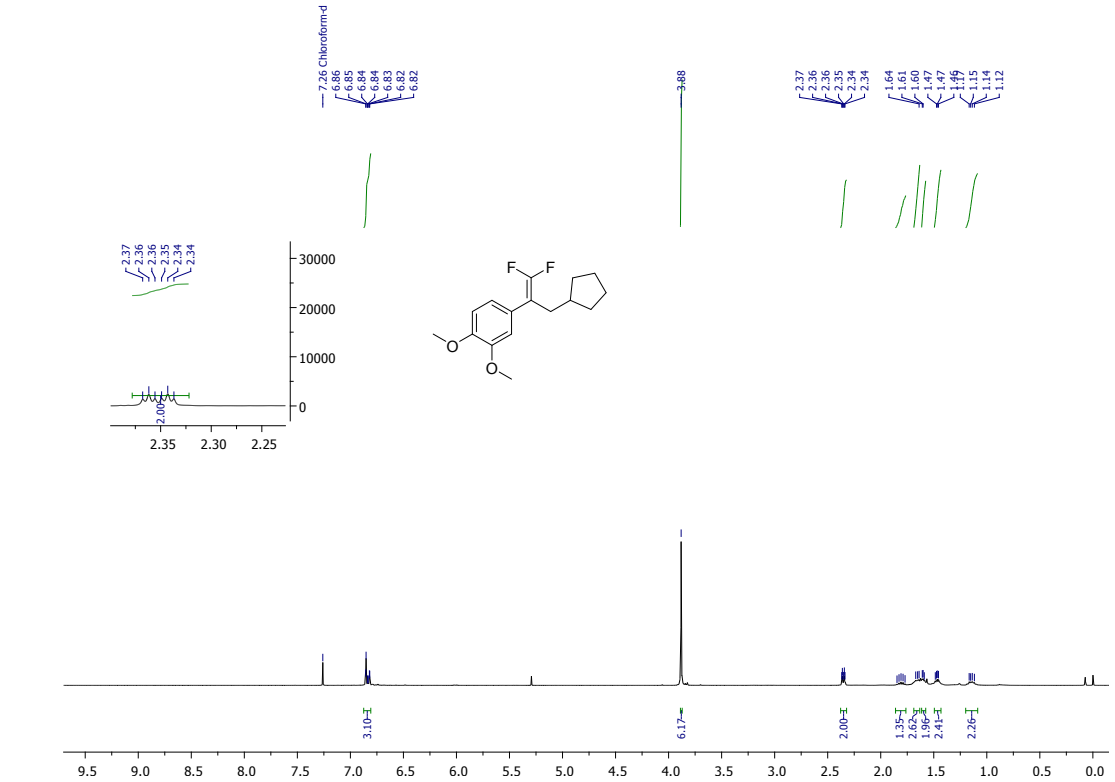
^{1}H NMR spectrum of 71



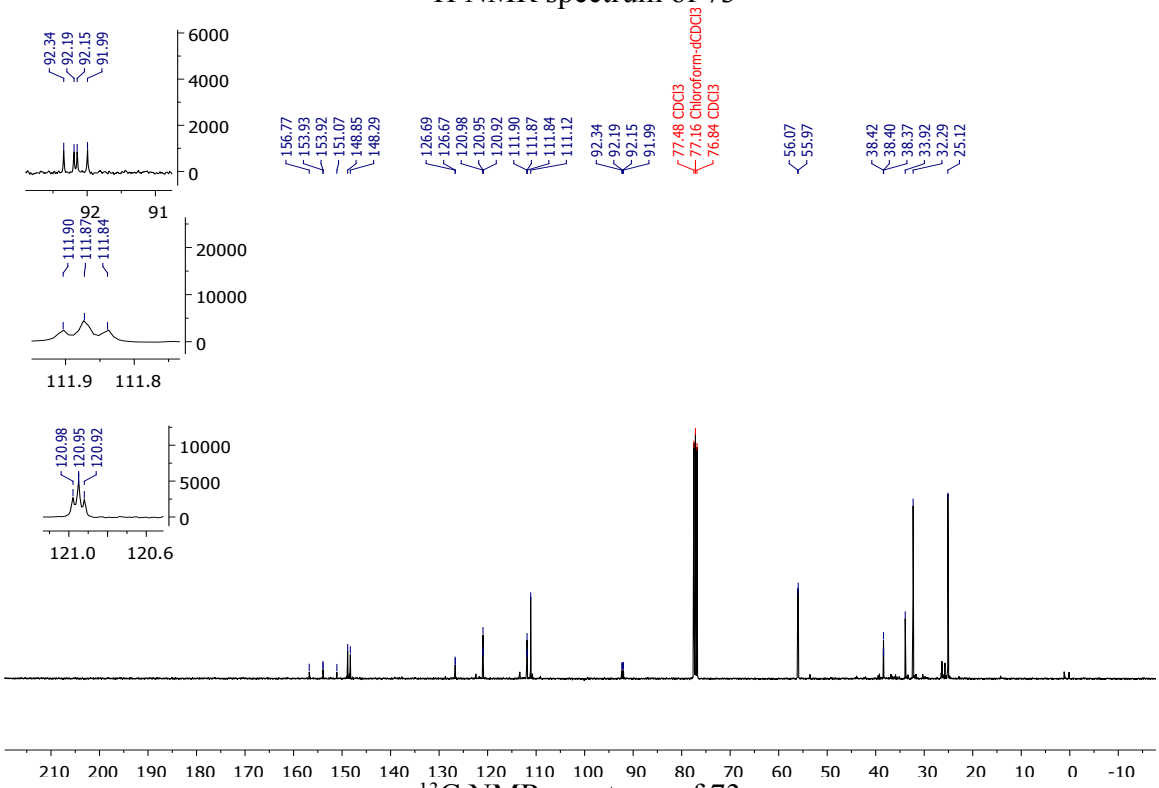
^{13}C NMR spectrum of 71



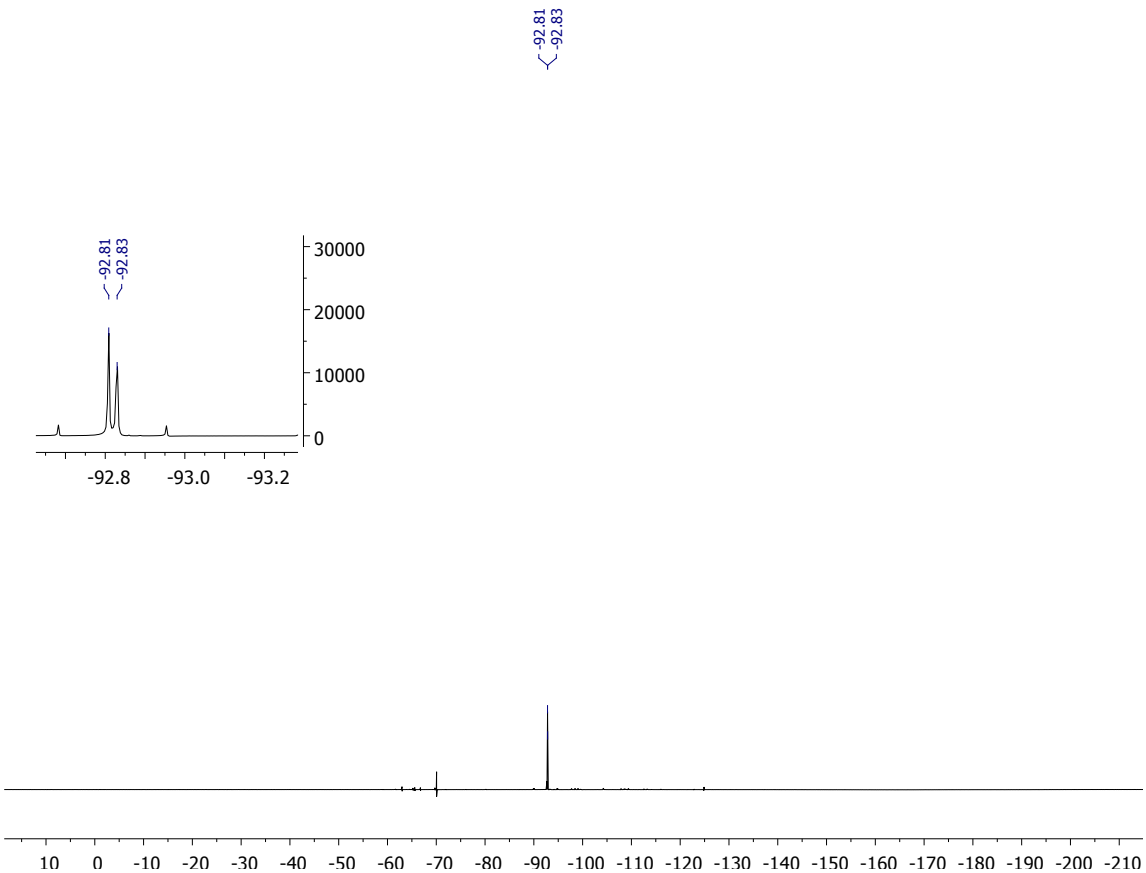
^{19}F NMR spectrum of 71



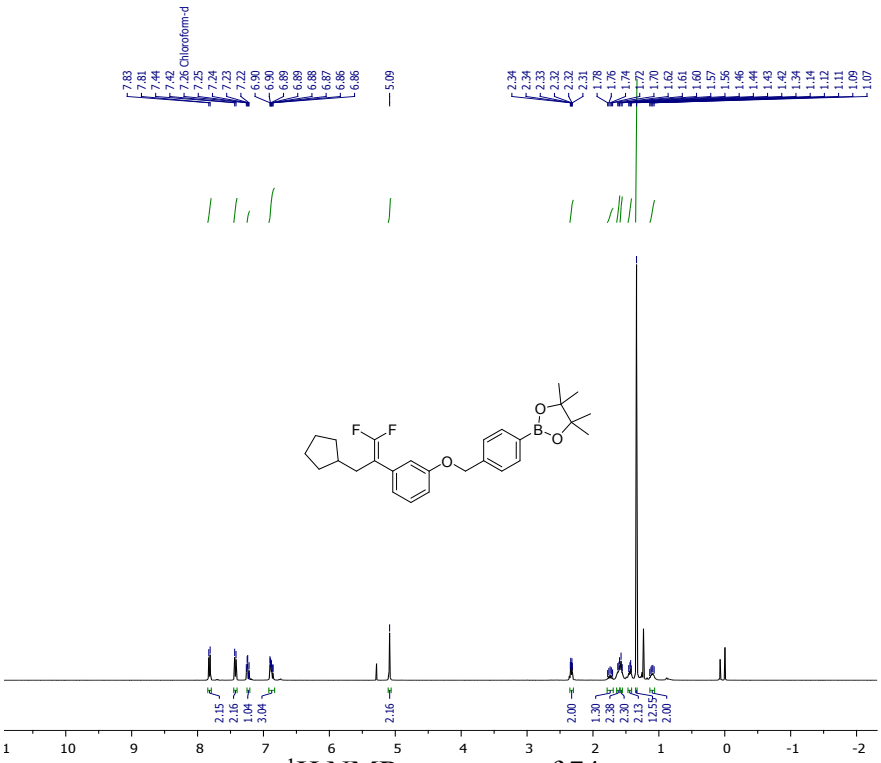
^{1}H NMR spectrum of 73



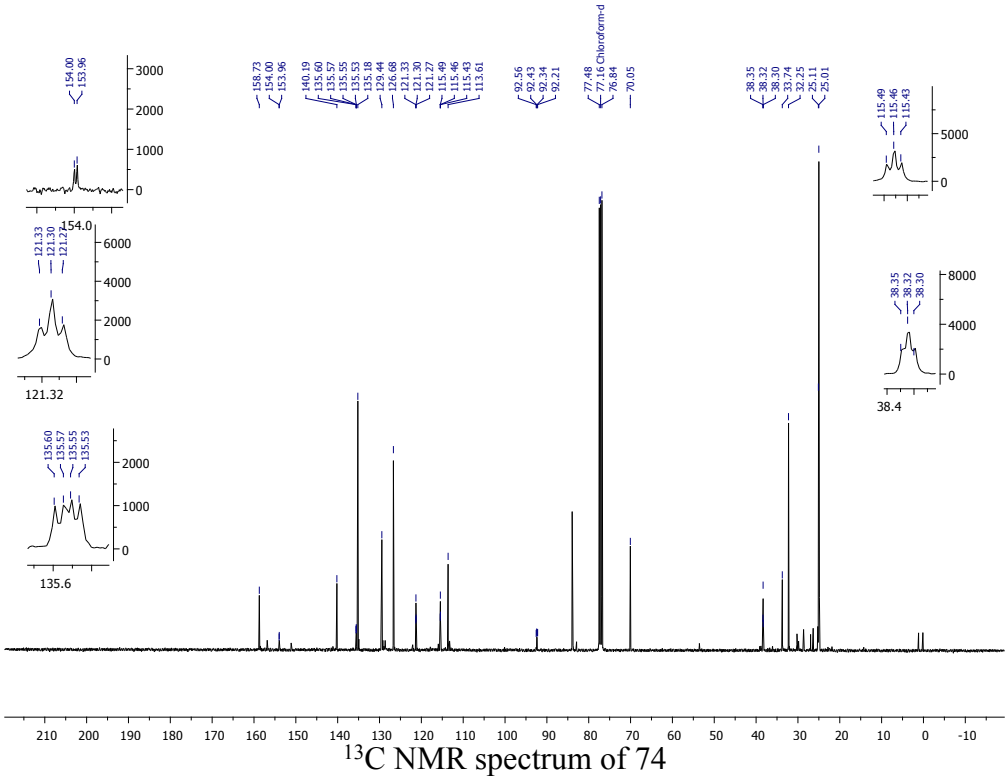
^{13}C NMR spectrum of 73



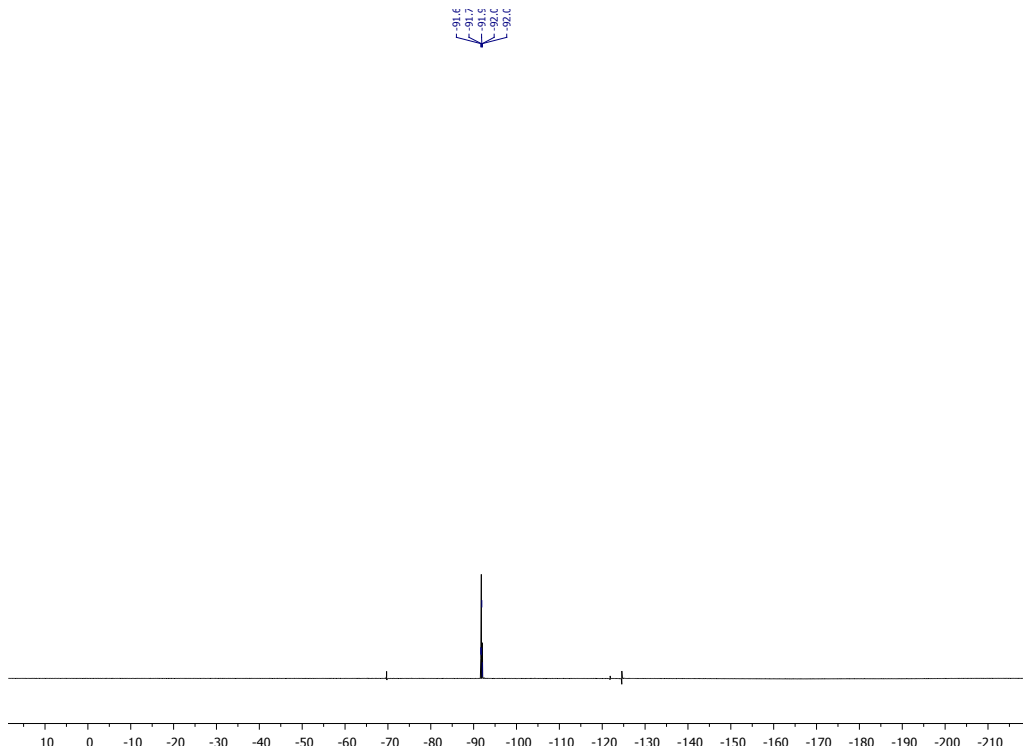
^{19}F NMR spectrum of 73



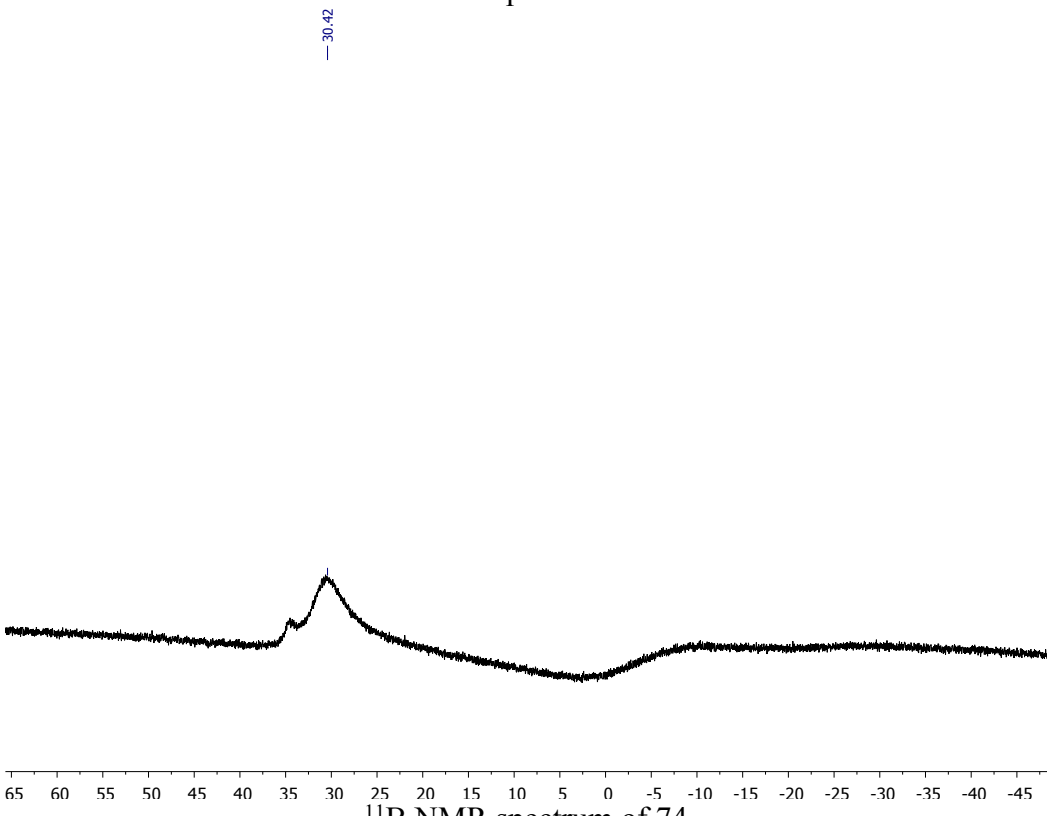
^{1}H NMR spectrum of 74



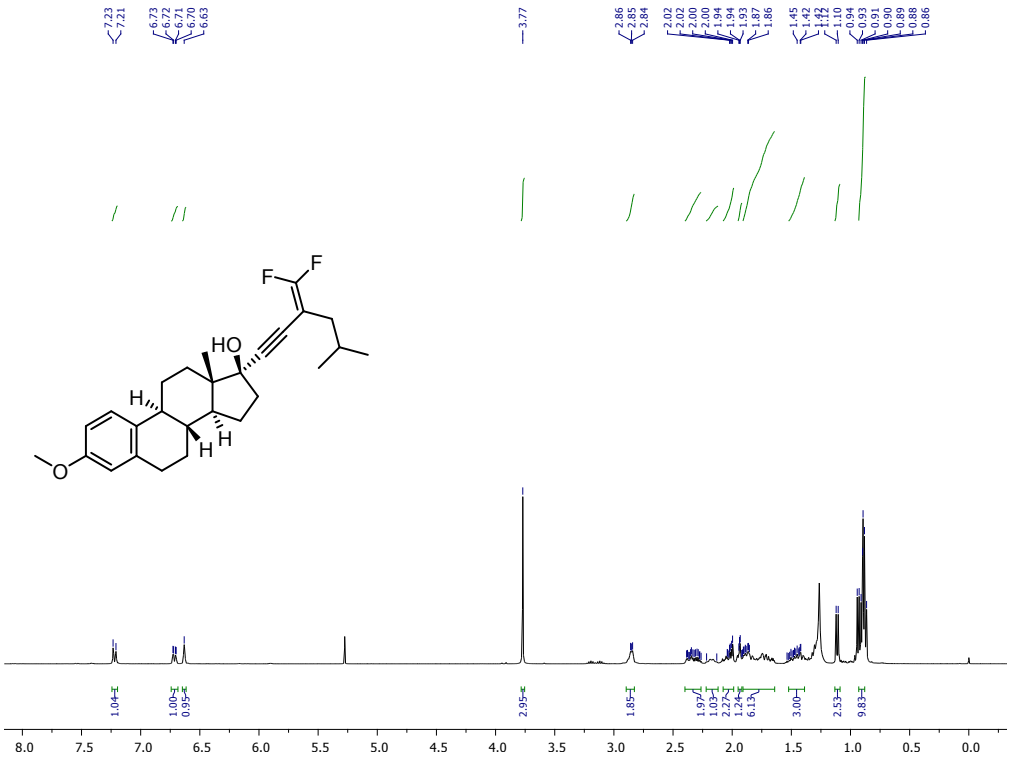
^{13}C NMR spectrum of 74



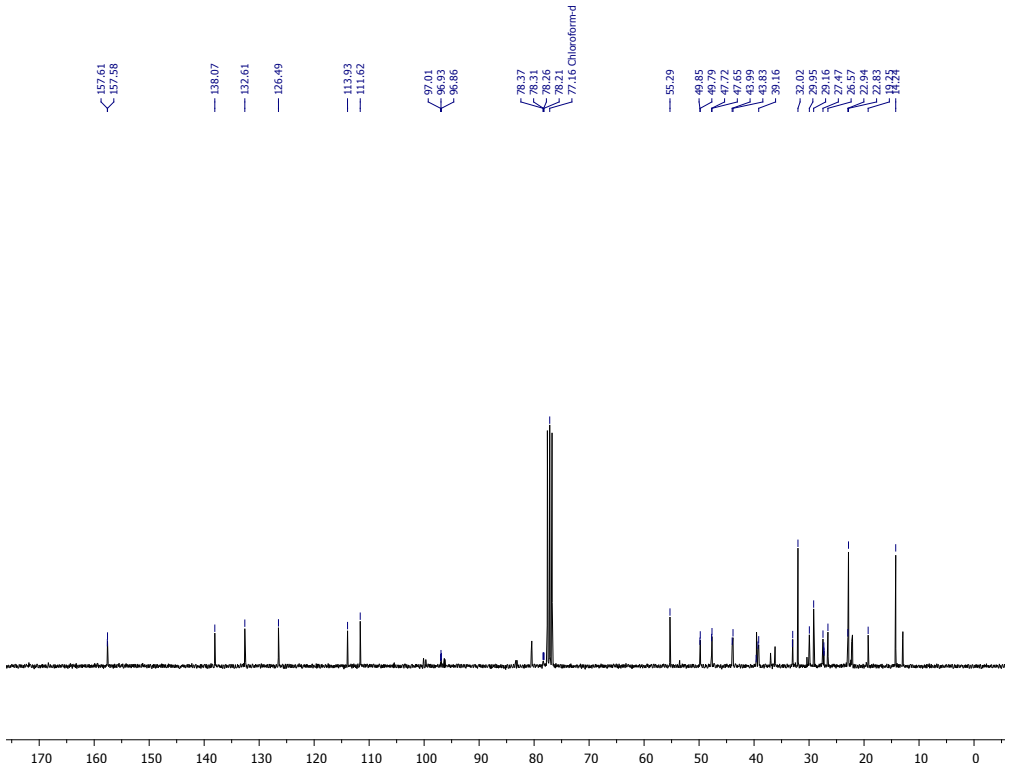
^{19}F NMR spectrum of 74



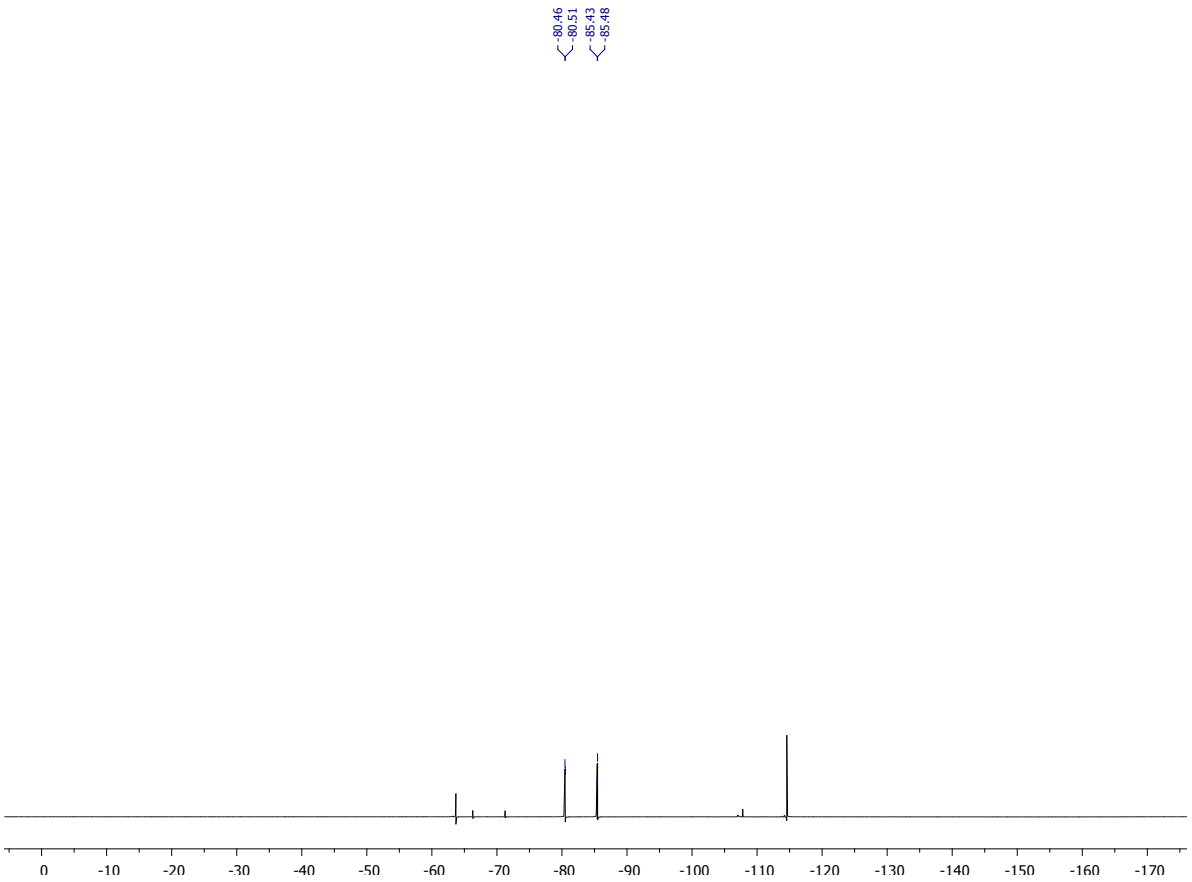
^{11}B NMR spectrum of 74



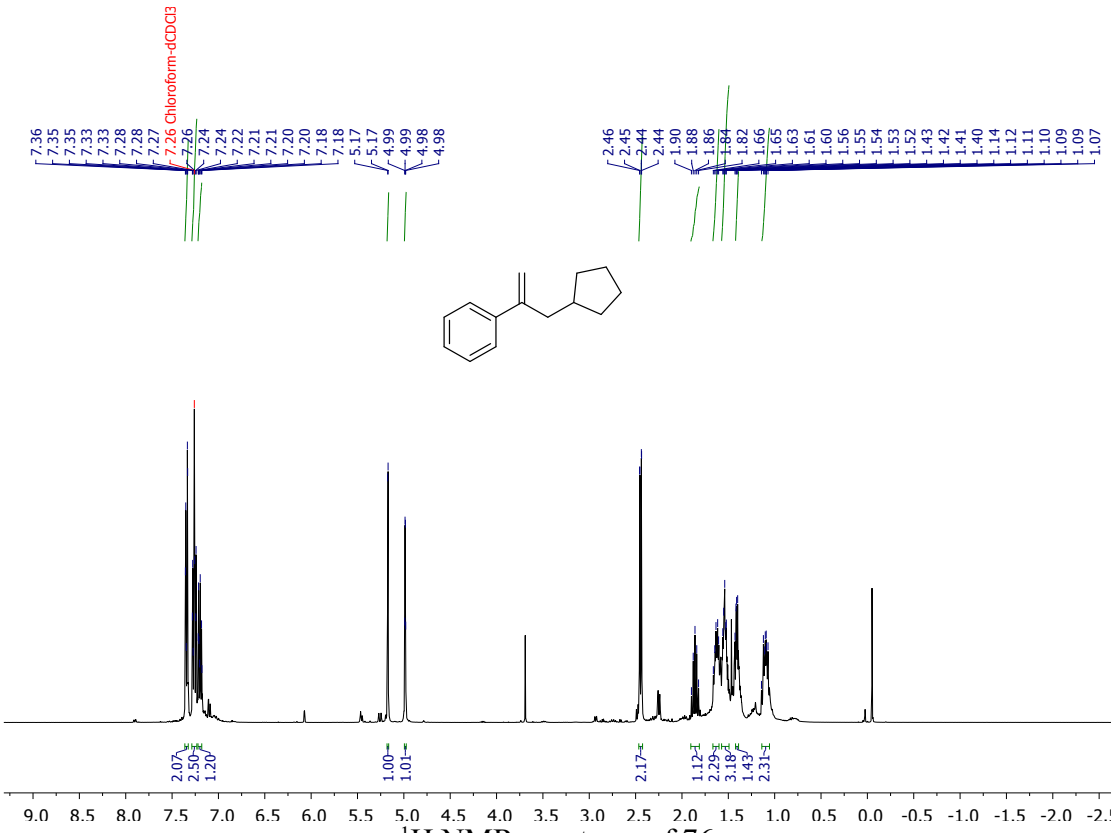
^{1}H NMR spectrum of 75



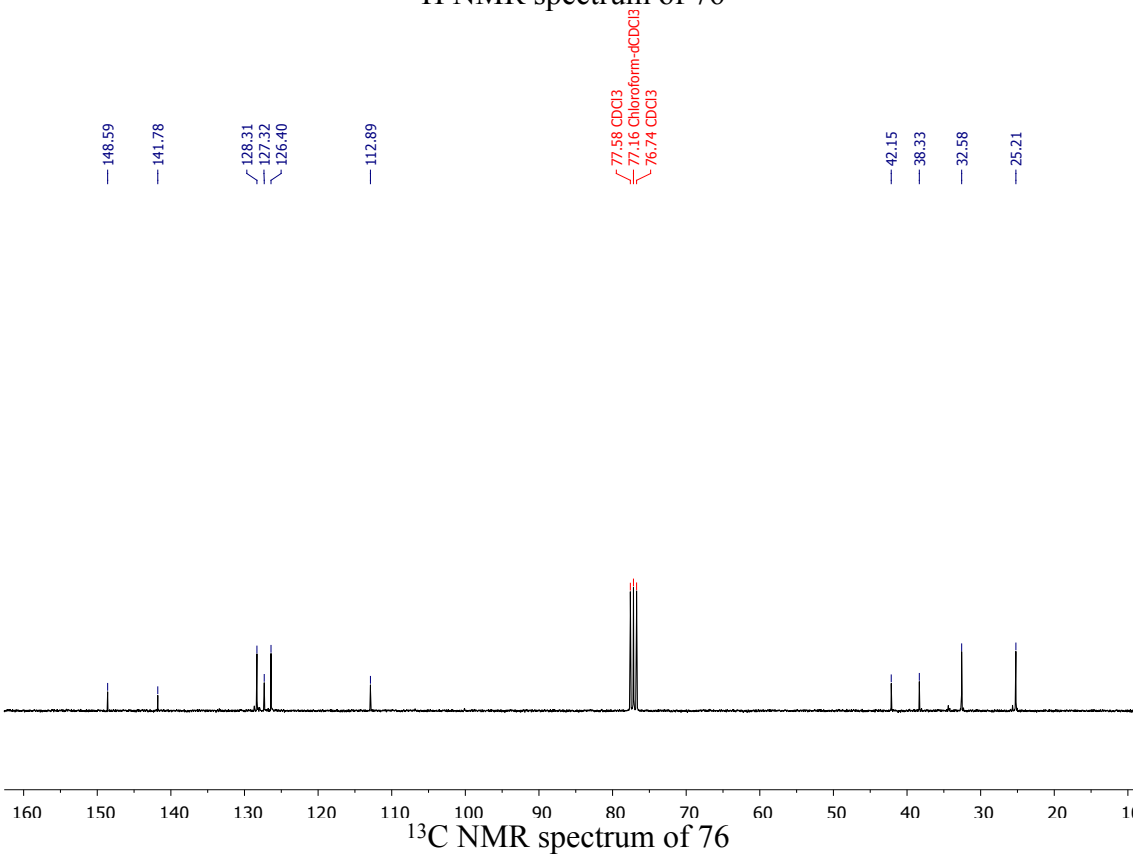
^{13}C NMR spectrum of 75



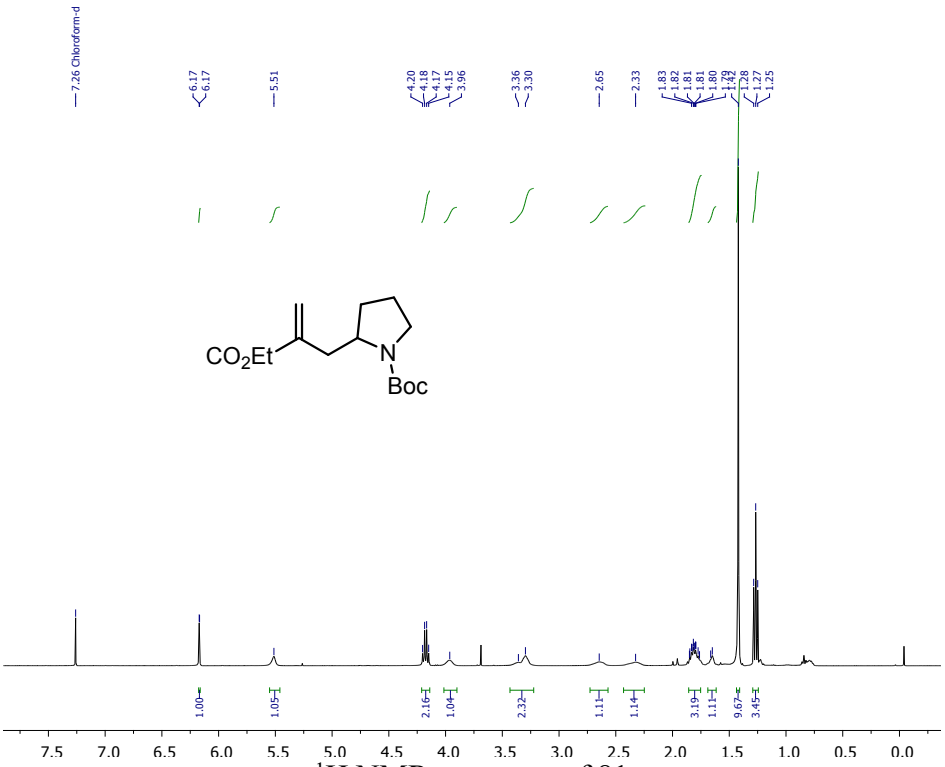
^{19}F NMR spectrum of 75



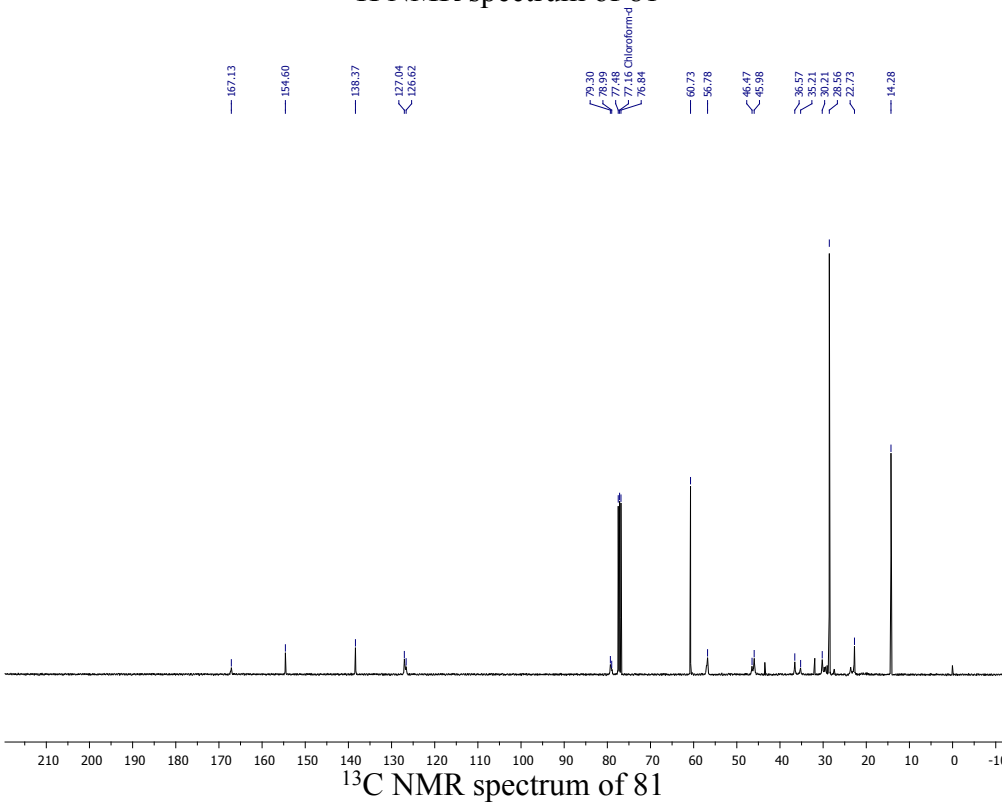
^{1}H NMR spectrum of 76



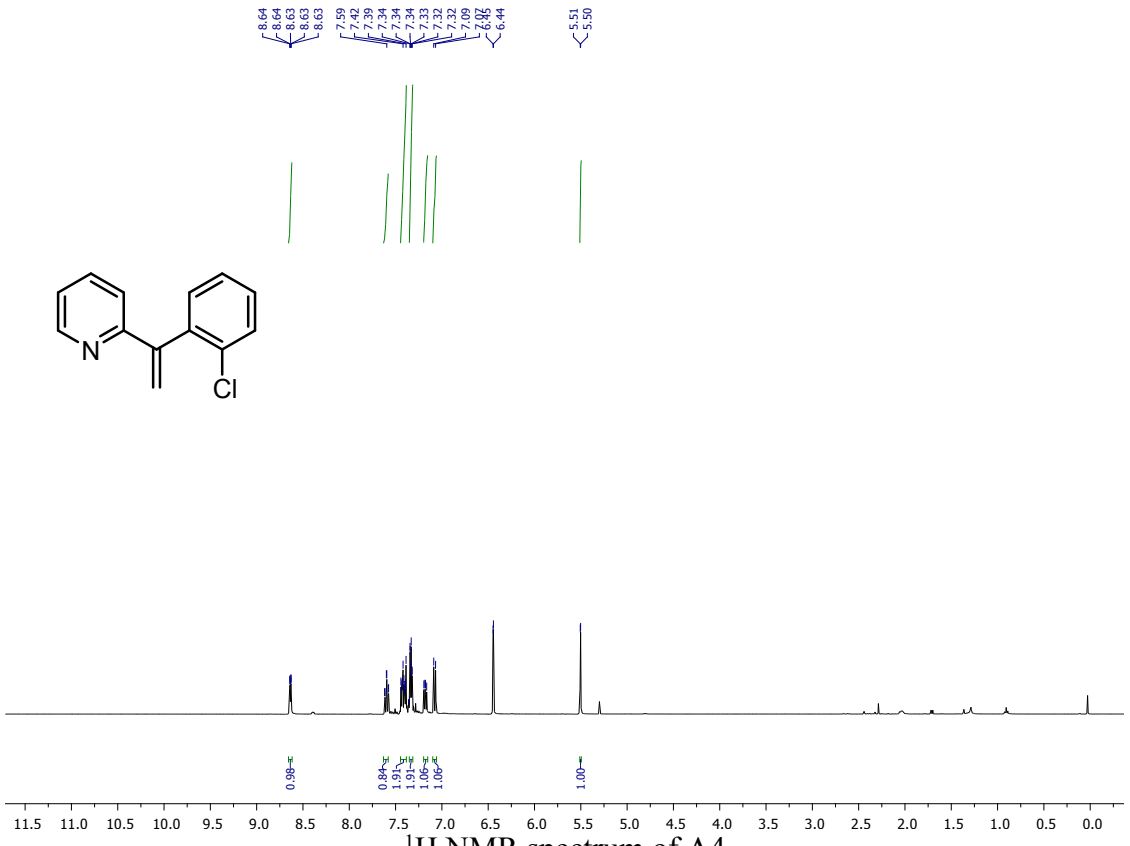
^{13}C NMR spectrum of 76



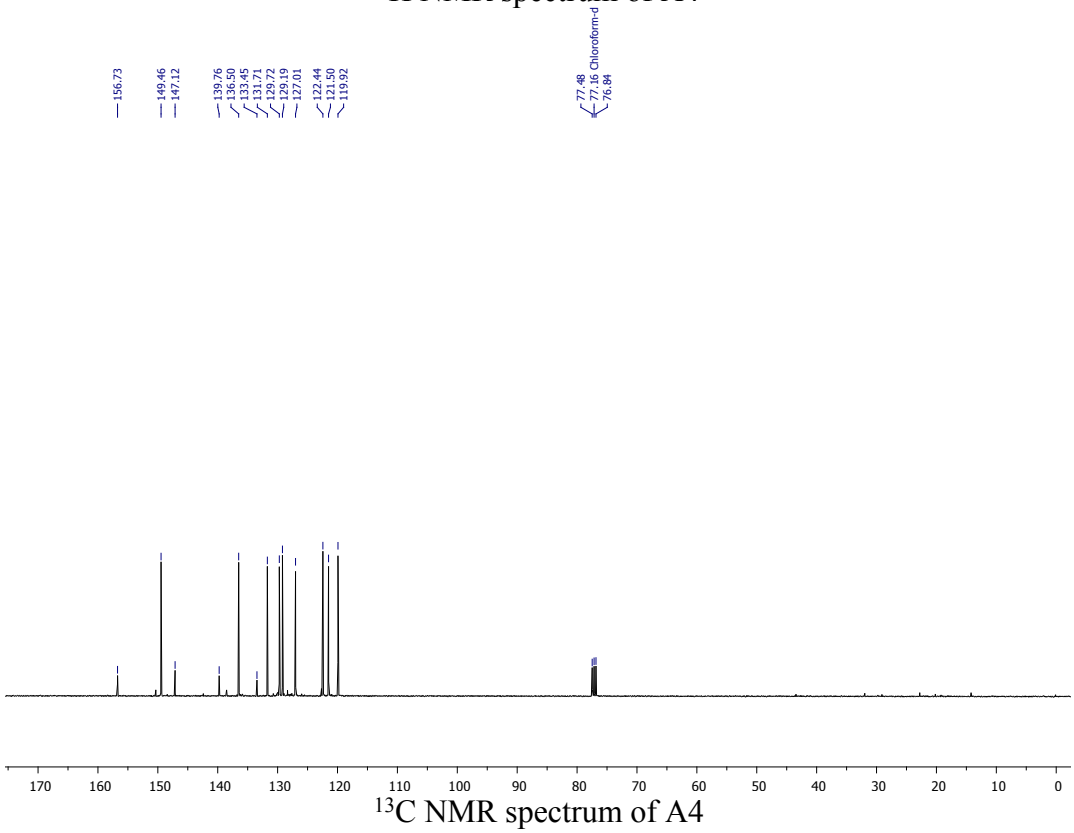
^{1}H NMR spectrum of 81



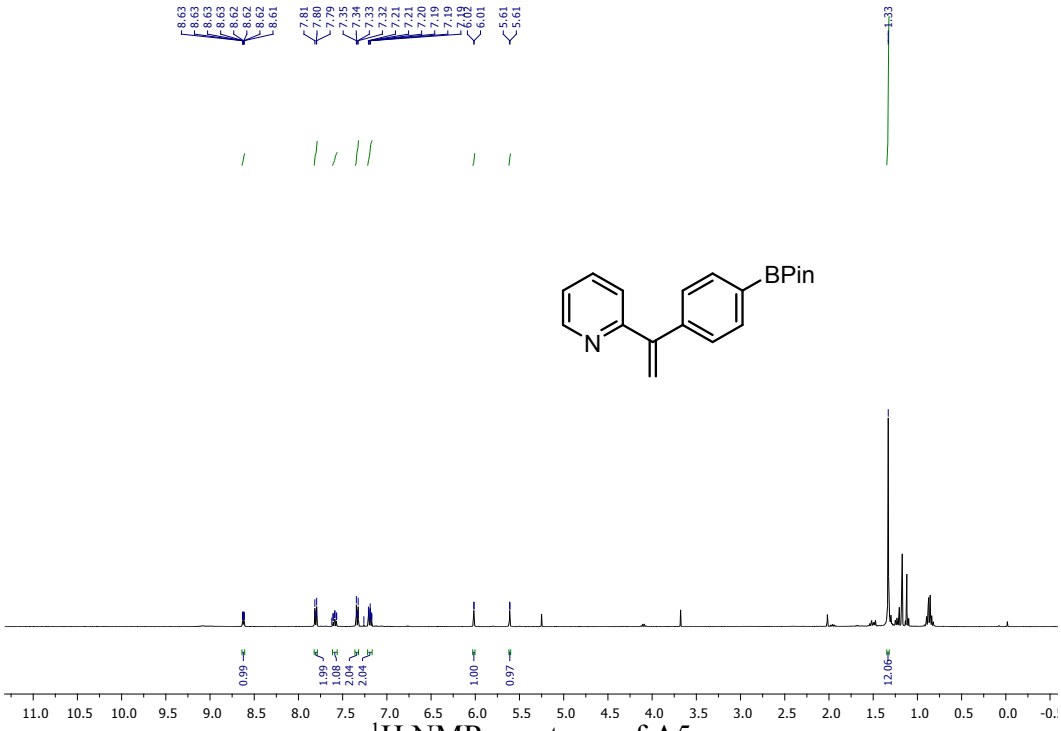
^{13}C NMR spectrum of 81



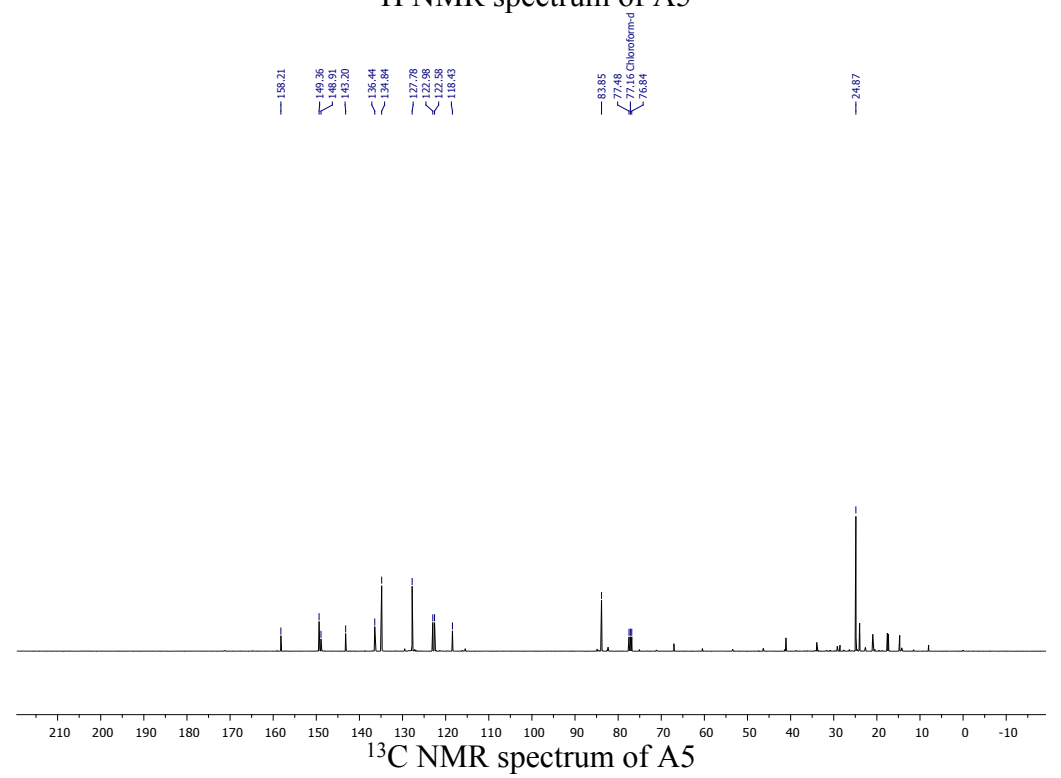
^{1}H NMR spectrum of A4



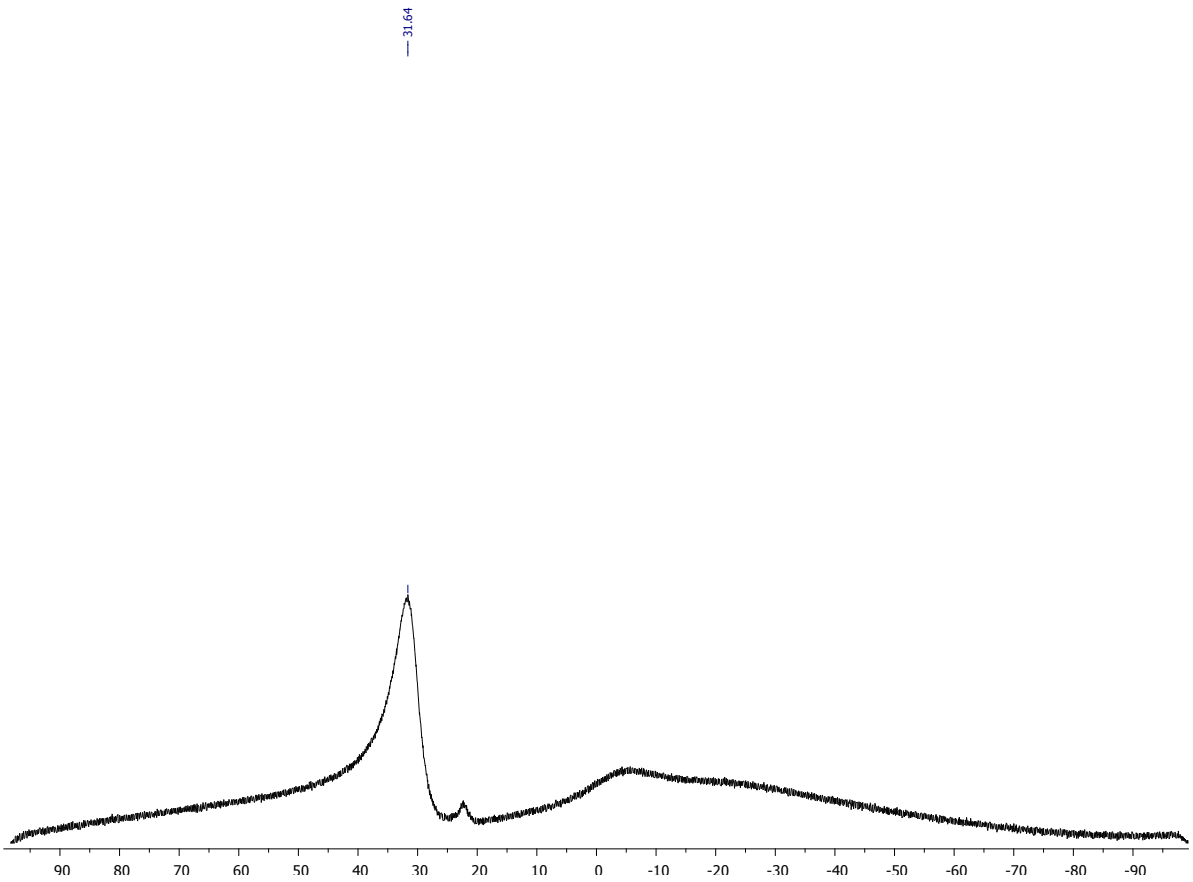
^{13}C NMR spectrum of A4



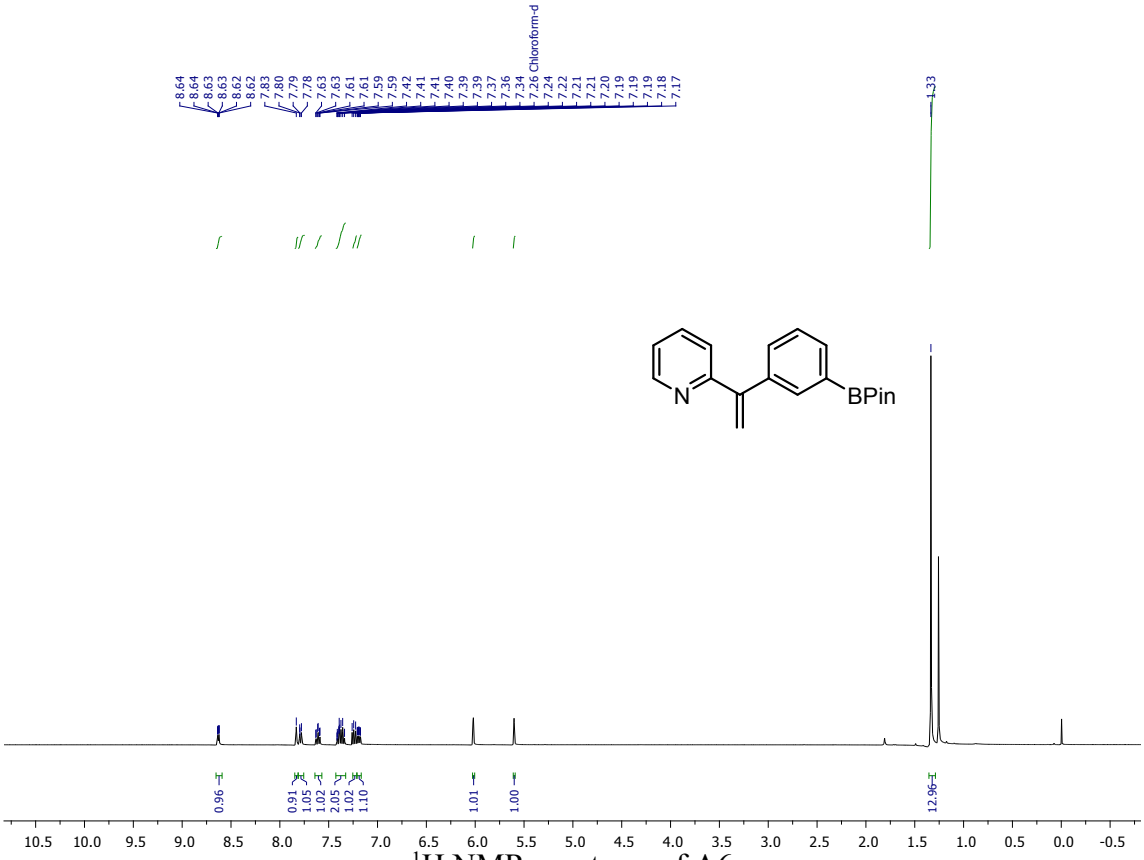
^{1}H NMR spectrum of A5



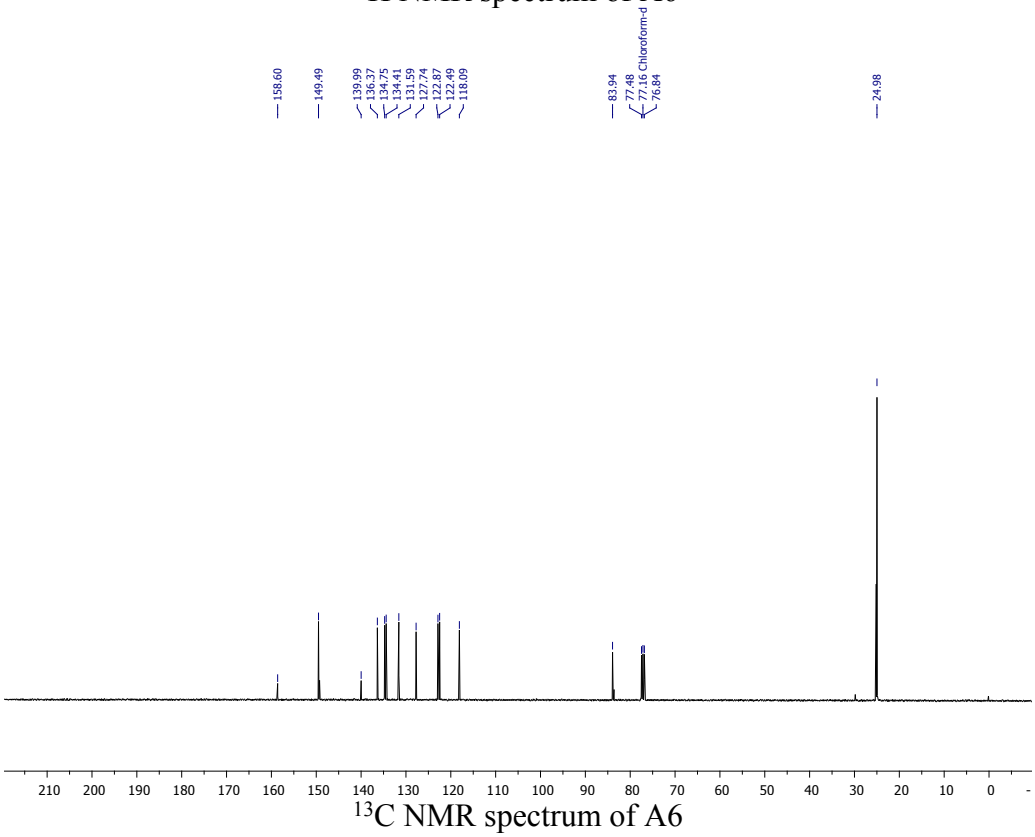
^{13}C NMR spectrum of A5



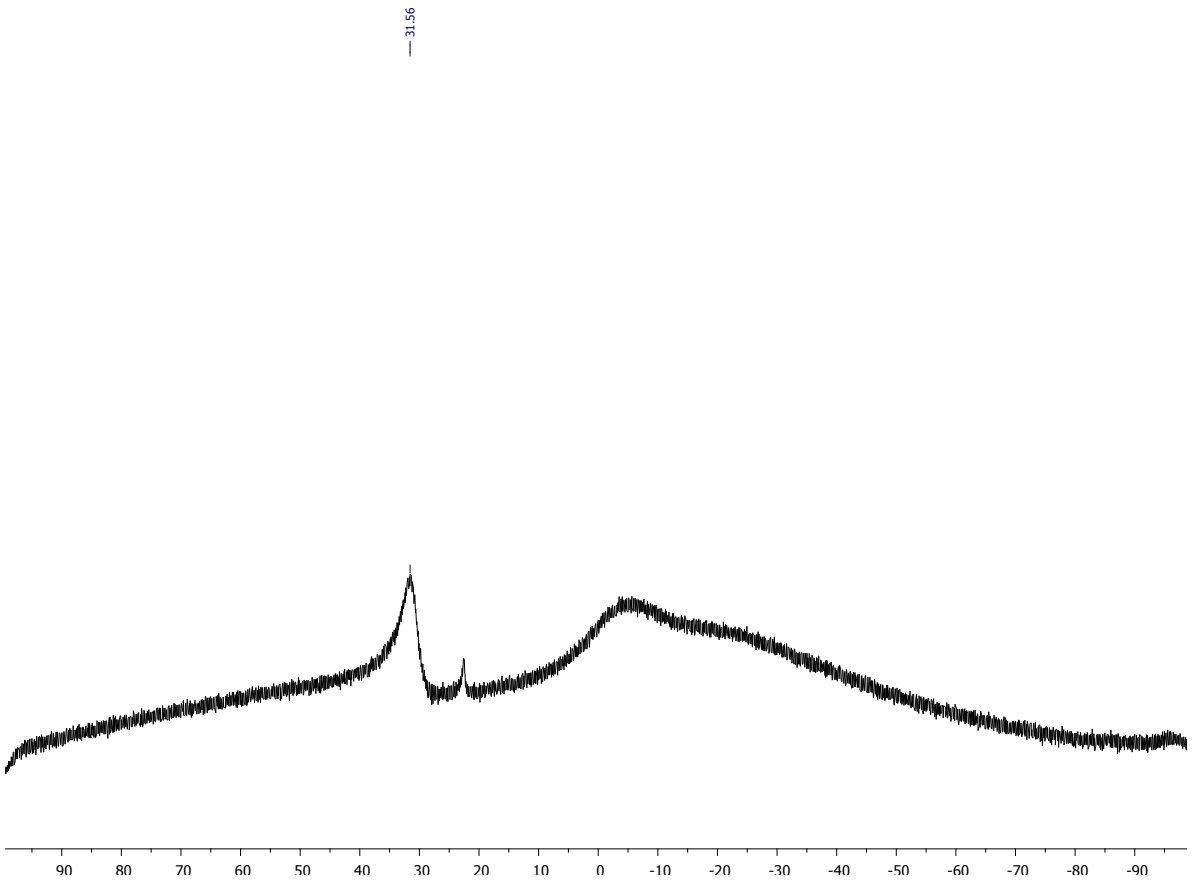
^{11}B NMR spectrum of A5



^{1}H NMR spectrum of A6



^{13}C NMR spectrum of A6



^{11}B NMR spectrum of A6

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