Supporting Information

N-allylbenzimidazole as a strategic surrogate in Rh-catalyzed stereoselective trans-propenylation of aryl C(sp^2)-H bond

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1. General Information:[1]

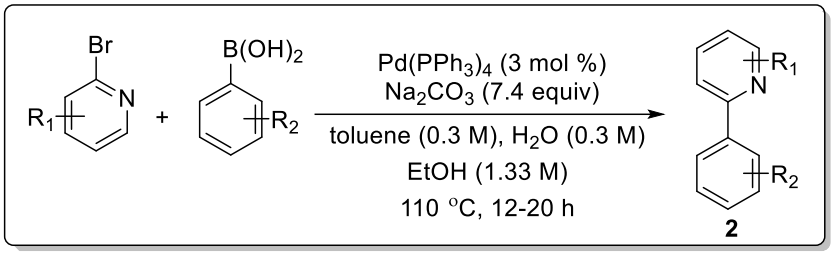
All the starting materials were bought from Sigma Aldrich, Alfa-Aesar, Avra, TCI and Spectrochem, and used without any further purification. For column chromatography, silica gel (100-200, 230-400 mesh) was used from Acme. A gradient elution using distilled hexane and ethyl acetate was performed, based on Merck aluminum TLC sheets. All isolated compounds were characterized by ^{1}H NMR (Bruker-400/700 MHz), ^{13}C NMR spectroscopy and HRMS. Copies of the ^{1}H NMR, ^{13}C NMR, ^{19}F NMR can be found in the Supporting Information. Nuclear Magnetic Resonance spectra were recorded on a Bruker 400/700 MHz instrument. HRMS signal analysis was performed using Bruker micro TOF Q-II mass spectrometer. X-ray analysis was conducted using Rigaku Smartlab X-ray diffractometer in NISER, Bhubaneswar. All ^{1}H NMR experiments were reported in parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent.[2] All ^{13}C NMR spectra were reported in ppm relative to $CDCl_3$ (77.36 ppm).[2] Chemical shift multiplicities have represented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, td = triplet of doublet. Allyl carbonates,[3] and 2-(2-propylphenyl)pyridine[4] were prepared by following literature reports.

Abbreviations:

EtOH = Ethanol, $NaHCO_3$ = Sodium bicarbonate, $[Cp^*RhCl_2]_2$ = 1,2,3,4,5-pentamethyl cyclopentadienyl rhodium (III) chloride dimer, Na_2CO_3 = Sodium carbonate, $Cu(OAc)_2$ = Copper acetate, TLC = Thin layer chromatography, $LiClO_4$ = Lithium perchlorate, $Zn(OAc)_2$ = Zinc acetate, EtOAc = Ethyl acetate, TFE = Trifluoroethanol, DCM = Dichloromethane, MeOH = Methanol, DMF = *N*,*N*-Dimethylformamide, D_2O = Deuterium oxide.

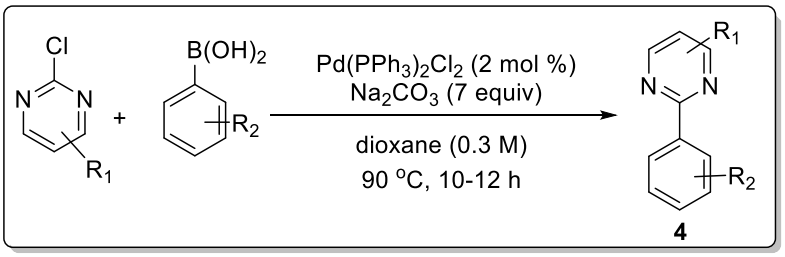
(2) Experimental procedure:

(2.1) Preparation of 2-Phenylpyridines[5]



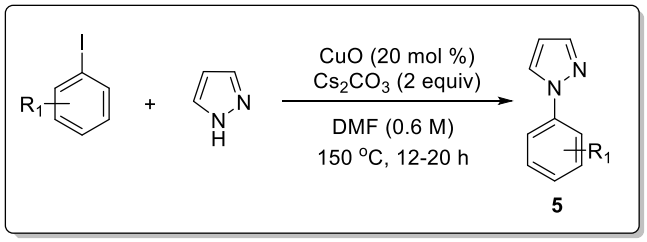
In an oven-dried 25 mL round-bottom flask, 2-bromopyridine (1 equiv, 1 mmol), toluene (0.33 M, 3.3 mL), H_2O (0.33 M, 3.3 mL), and EtOH (1.33 M, 0.75 mL) were taken. To this solution, aryl-boronic acid (1.3 equiv, 1.3 mmol), Na_2CO_3 (7.4 equiv, 7.4 mmol), and $Pd(PPh_3)_4$ (0.03 equiv, 3 mol %) were added. Then, the reaction mixture was refluxed at 110 °C until the completion of starting material (as monitored by TLC). After completion of the reaction (12-20 h), the reaction mixture was cooled down to room temperature and was quenched with saturated NH_4Cl. The reaction mixture was extracted with EtOAc and washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and then purified through column chromatography (100-200 mesh silica, eluant: hexane/EtOAc) giving the desired phenylpyridines **2**.

(2.2) Preparation of 2-Phenylpyrimidines[6]



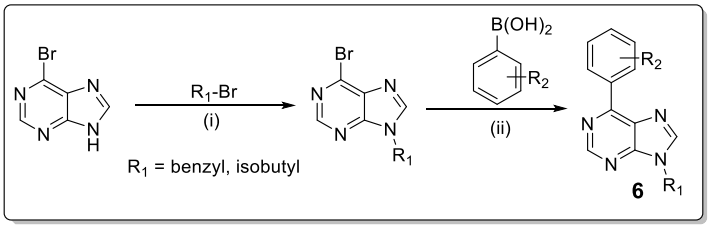
To an oven-dried 25 mL round bottom flask, 2-bromopyrimidine (1 equiv, 1 mmol), aryl boronic acid (1.2 equiv, 1.2 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 equiv, 2 mol %), Na_2CO_3 (7 equiv, 7 mmol), and dioxane (0.33 M, 3.3 mL) were added. The reaction mixture was heated at 90 °C until the 2-chloropyrimidine was consumed completely (monitored by TLC). The residue was diluted with EtOAc (30 mL), washed with H_2O (30 mL) and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified by column chromatography on silica gel (100-200 mesh silica, eluant: hexane/EtOAc) to afford the arylpyrimidines **4**.

(2.3) Preparation of 1-Phenylpyrazoles[7]



A solution of aryl iodide (1 equiv, 1 mmol), pyrazole (2 equiv, 2 mmol), CuO (0.2 equiv, 0.2 mmol), and Cs_2CO_3 (2 equiv, 2 mmol) in anhydrous DMF (0.6 M, 1.66 mL) was stirred at 150 °C up to completion of the reaction (monitored by TLC). After the completion of the reaction (12-20 h), the reaction mixture was filtered, and the solid was washed with dichloromethane. The filtrate was extracted with water. The organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuum. The crude was purified by column chromatography on silica gel (100-200 mesh silica gel, eluant: hexane/EtOAc) to get desired arylpyrazoles **5**.

(2.4) Preparation of 6-(4-chlorophenyl)-purines[8]

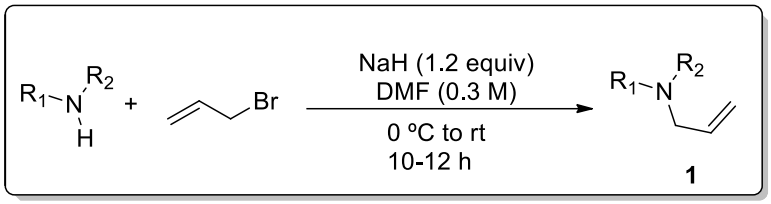


(i) Potassium carbonate (3 equiv, 3 mmol) was added to a continuously stirring solution of 6-bromopurine (1 equiv, 1 mmol) in anhydrous DMF (0.1 M, 10 mL) at ambient temperature under N_2. After 20 min, alkyl bromide (1.5 equiv, 1.5 mmol) was added. The resulting mixture was stirred for 12 h, filtered, and evaporated in vacuo. N-protected-6-bromopurines were obtained after column purification (100-200 silica gel) using EtOAc/hexane eluent system.

(ii) In an oven-dried 25 mL round-bottom flask, N-protected-6-bromopurines (1 equiv, 1 mmol), toluene (0.33 M, 3.3 mL), H_2O (0.33 M, 3.3 mL), and EtOH (1.33 M, 0.75 mL), were taken. To this solution, aryl-boronic acid (1.3 equiv, 1.3 mmol), Na_2CO_3 (7.4 equiv, 7.4 mmol), and $Pd(PPh_3)_4$ (0.3 equiv, 3 mol %) were added. Then, the reaction mixture was refluxed at 110 °C. After completion of the reaction (as monitored by TLC), the reaction mixture was cooled down to room temperature and was quenched with saturated NH_4Cl. The reaction mixture was extracted with EtOAc and washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and then purified through column

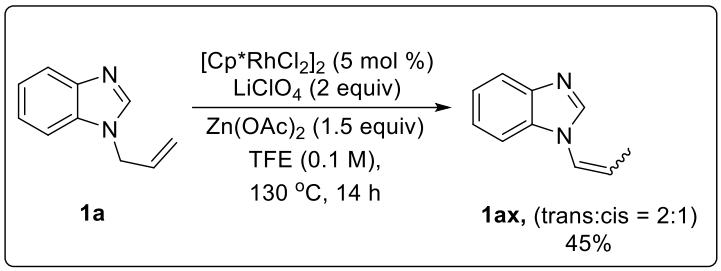
chromatography (100-200 mesh silica gel, eluant: hexane/EtOAc) giving the desired 9-alkyl-6-(4-chlorophenyl)-purines **6**.

(2.5) Preparation of *N*-allylamines

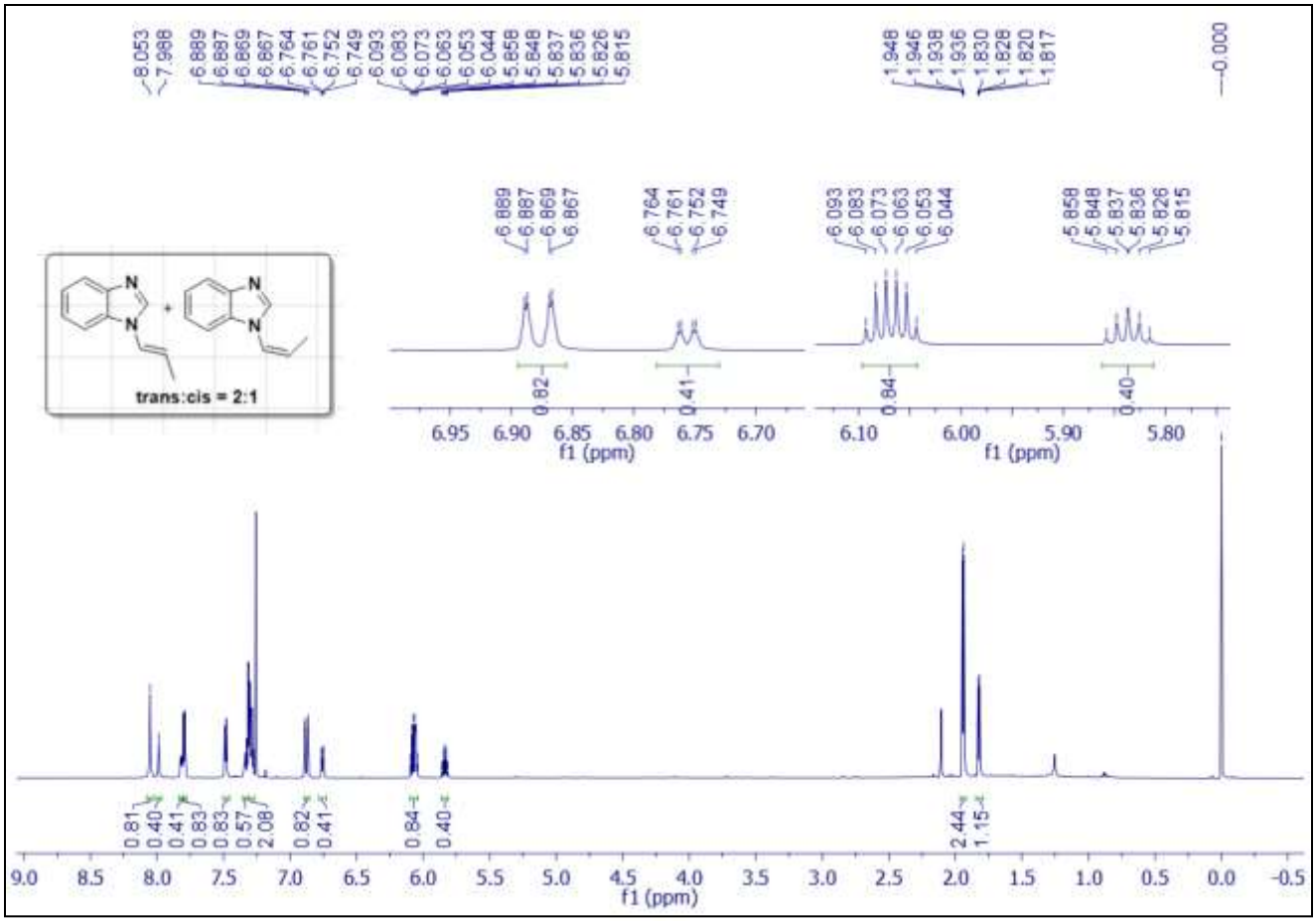


To an oven-dried 25 mL round bottom flask, charged with a magnetic stir bar, amines/indole/benzimidazole (1 equiv, 0.5 mmol) and anhydrous DMF (0.3 M, 1.66 mL) were taken under a nitrogen atmosphere. The solution was cooled to 0 °C. Then, NaH (1.2 equiv, 0.6 mmol) was added and stirred for 30 min. To this solution, allyl bromide (1.1 equiv, 5.5 mmol) was added dropwise and allowed to stir at room temperature up to the completion of the reaction (monitored by TLC, 2-3 h). After completion, the reaction mixture was washed with ice-cold brine and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4, concentrated under vacuum, and purified by column chromatography to get corresponding *N*-allyl derivatives **1**.

(2.6) Preparation of internal alkene 1ax



To an oven-dried 25 mL Schlenk tube charged with a magnetic stir bar, $LiClO_4$ (0.76 mmol, 2 equiv) was added and heated under reduced pressure to eliminate a trace of moisture. To this tube, alkene **1a** (0.38 mmol, 1 equiv), $[Cp^*RhCl_2]_2$ (0.02 mmol, 5 mol %), $Zn(OAc)_2$ (0.57 mmol, 1.5 equiv), and TFE (0.1 M, 3.8 mL) were added under nitrogen atmosphere. The reaction mixture was stirred (750 rpm) in a preheated aluminum block at 130 °C. Progress of the reaction was monitored by TLC. After 14 h, the reaction mixture was cooled to room temperature and was transferred into a 25 mL round bottom flask. The solvent was removed under reduced pressure. The crude mixture was purified by column chromatography to get the internal alkene **1ax** as a colorless oil (28 mg, 45% yield). The ratio (*trans* to *cis*) of alkene was calculated from ^{1}H-NMR spectrum.

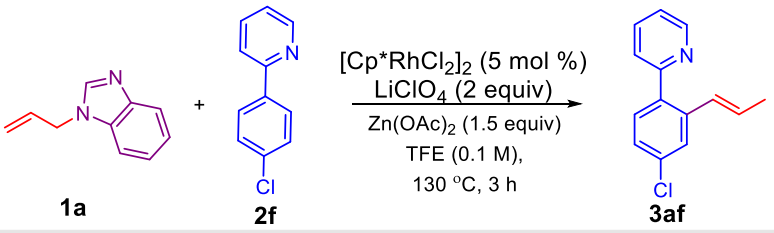


(2.7) Optimization of reaction conditions (Table S1):

Our investigation began with the reaction of *N*-allyl benzimidazole **1a** and 2-(4-chlorophenyl) pyridine **2f** (Table S1). We were delighted to find that 5 mol % of Cp*Rh catalyst and 2 equiv. of $LiClO_4$ in combination with 1.5 equiv of $Zn(OAc)_2$ gave mono-propenylated product **3af** in 75% of yield (Table S1, entry 1). The use of a cationic Rh-complex resulted in 31% yield of **3af** (Table S1, entry 2), whereas $Rh_2(OAc)_4$ dimer and Wilkinson's catalyst failed to deliver the product (Table S1, entries 3-4). When solvents other than TFE were screened, lower yields were observed (Table S1, entries 5-7). These results suggest that the protic solvent TFE plays a crucial role in the reaction. It has been reported that the use of water can enhance the hydrolysis of C-N bonds.[18] Therefore, to enhance the rate of C-N bond cleavage of *N*-allylbenzimidazole, a 1:1 ratio of TFE:H_2O was explored (Table S1, entry 8), but instead of improved yield, we observed only a trace amount of product. We have also screened the reaction at lower temperatures however, lower yields were observed (Table

S1, entries 9-11). $LiClO_4$ works well for this protocol, replacing it with costly silver additives such as $AgSbF_6$ and AgOAc, resulting in no reaction (Table S1, entries 12-13).

Table S1: Optimization of reaction conditions



1a **2f** **3af**

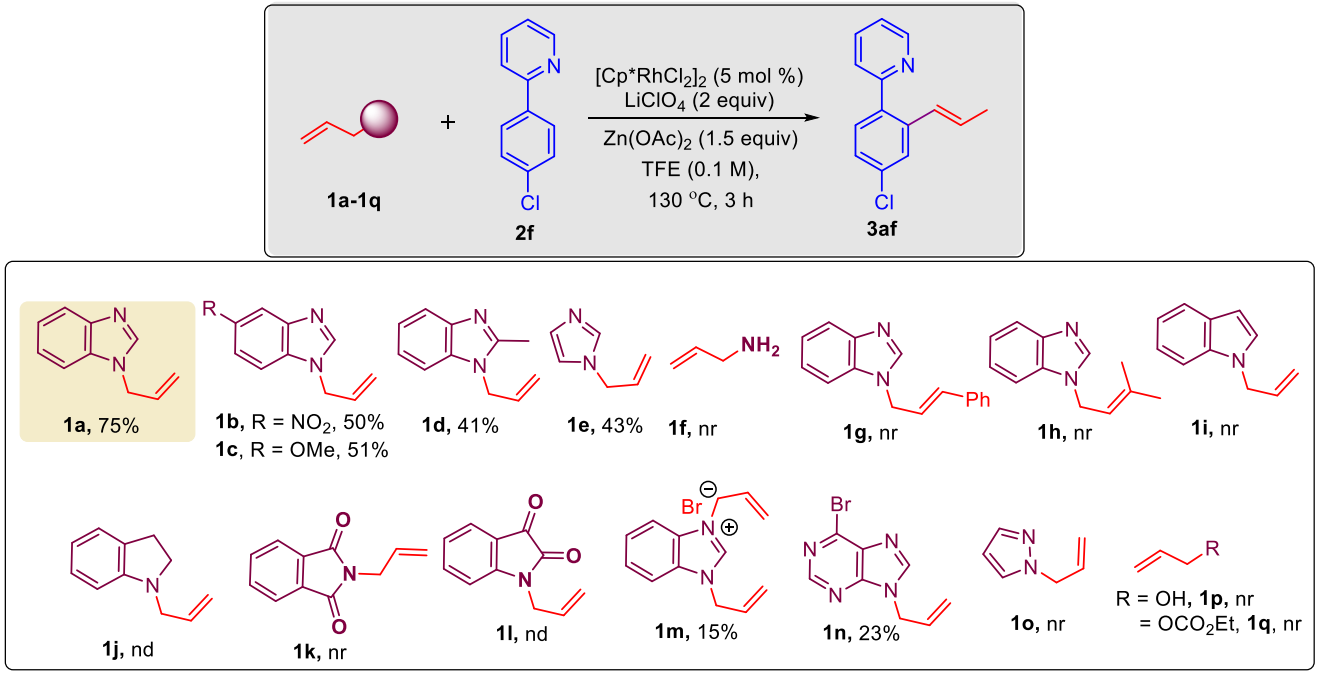
entry	deviation from the standard conditions	yield of **3af**(%)[b]
1	**none**	**75**
2	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	31
3	$Rh_2(OAc)_4$	nr
4	$Rh(PPh_3)_3Cl$	nr
5	MeOH	25
6	HFIP	20
7	TFT	nr
8	TFE+H_2O	trace
9	temperature 70 °C instead of 130 °C	nr
10	temperature 90 °C instead of 130 °C	trace
11	temperature 110 °C instead of 130 °C	40
12[c]	$AgSbF_6$ instead of $LiClO_4$	nr
13[c]	AgOAc instead of $LiClO_4$	nr
14	$NaIO_4$ instead of $LiClO_4$	20
15	**1a** (1 equiv) instead of 3 equiv	22
16	**1a** (2 equiv) instead of 3 equiv	46
17	$Zn(OTf)_2$ instead of $Zn(OAc)_2$	60
18	PivOH instead of $Zn(OAc)_2$	trace
19	$Cu(OTf)_2$ instead of $Zn(OAc)_2$	nr
20	2 h	35
21	4 h	73
22	6 h	20
23	without [Rh]	nr
24	without $LiClO_4$	trace
25[d]	without $Zn(OAc)_2$	55 (12 h)

[a]Reaction conditions: **2f** (1 equiv, 0.06 mmol), **1a** (3 equiv, 0.18 mmol), $[Cp^*RhCl_2]_2$ (5 mol %, 0.003 mmol), $LiClO_4$ (2 equiv, 0.12 mmol), $Zn(OAc)_2$ (1.5 equiv, 0.09 mmol), TFE (0.1 M, 0.6 mL), 130 °C, N_2, [b]Isolated yield. [c]20 mol% of silver additives were used, [d]Isolated yield after 12 h.

In addition, the use of $NaIO_4$ in place of $LiClO_4$ resulted in only a 20% yield of the product **3af** (Table S1, entry 14). Varying the equivalents of *N*-allyl benzimidazole resulted in lower yields (Table S1, entries 15-16). Further screening of Lewis and protic acid additives – $Zn(OTf)_2$, PivOH, and $Cu(OTf)_2$

– did not result in an improved yield of **3af** (Table S1, entries 17-19). To determine the effect of time, three parallel reactions were performed, and it was observed that after 4 h the product begins to decompose under the reaction conditions (Table S1, entries 20-22). Finally, control experiments confirmed the necessity of catalyst $[Cp^*RhCl_2]_2$, additive $LiClO_4$, and $Zn(OAc)_2$ (Table S1, entries 23-25). From these results, it is clear that $LiClO_4$ may be acting as a halide scavenger as well as a Lewis acid.

(2.8) Screening of allyl reagents (Table S2):

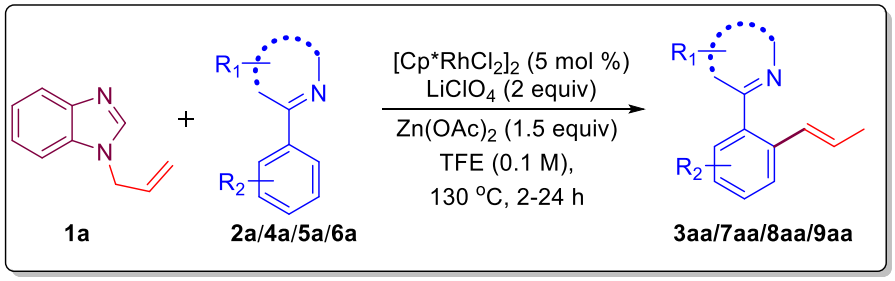


With the optimized conditions in hand, we proceeded to study the electronic influence of the *N*-allyl coupling partner on the C-H alkenylation of 2-arylpyridine **2f**. When **1a** contains either a π-electron-withdrawing group (EWG) such as $-NO_2$ (**1b**) or an electron donating group (EDG) such as -OMe (**1c**), similar reactivity was observed; both yielded ~50% of **3af**, indicating that the nature of the substituent in the benzenoid system has no remarkable impact. Similarly, when 2-methyl-*N*-allylbenzimidazole **1d** was taken as an alkenylating source, **3af** was obtained in 41% yield. Further, to check the influence of the benzenoid ring, *N*-allyl imidazole **1e** and allylamine **1f** were used instead of **1a**, while *N*-allyl imidazole gave 43%, and allylamine didn't give any product. These results imply that the presence of the benzene ring facilitates this transformation. Monosubstituted or disubstituted alkenes (**1g** and **1h**) could not deliver the respective alkenylated products, indicating that alkene

insertion into the Rh-C bond is subject to steric constraints and occurs prior to C-N bond cleavage. To check the role of the N3 nitrogen atom of **1a**, *N*-allyl indole **1i** was employed as the coupling partner. In this case, we did not observe any product **3af**, suggesting that the reaction is facilitated by interaction with the N3 atom of **1a** (likely binding with Lewis acid). Further, *N*-allyl indoline **1j** was also tested and found to be ineffective for this transformation. When the more electron-deficient *N*-allyl phthalimide **1k** and *N*-allyl isatin **1l** were used, product **3af** was not observed. The use of 1,3-diallylbenzimidazole **1m** and *N*-allyl-4-bromopurine **1n** gave mixtures of alkenylated and allylated products in poor yields. In contrast to imidazole **1e**, *N*-allyl pyrazole **1o** did not give the product **3af**. Moreover, when aryl pyridine **2f** was subjected to the standard reaction conditions with the more frequently used allylating reagents such as allyl alcohol **1p** and allyl ethyl carbonate **1q**, none of them produced either C-H allylated or alkenylated products. These studies confirm the efficiency and selectivity of *N*-allyl benzimidazole **1a** for a highly selective transformation.

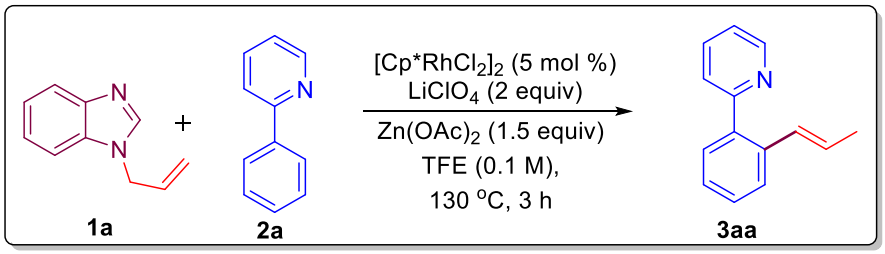
(3) General reaction procedures:

(3.1) General reaction procedure for Rh-catalyzed alkenylation reaction



To an oven-dried 25 mL Schlenk tube charged with a magnetic stir bar, $LiClO_4$ (0.2 mmol, 2 equiv) was added and heated under reduced pressure to eliminate a trace of moisture. To this tube, phenylpyridine **2** / phenyl pyrimidine **4** / phenylpyrazole **5** / 9-alkyl-6-(4-chlorophenyl)-purines **6** (0.1 mmol, 1 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 5 mol %), $Zn(OAc)_2$ (0.15 mmol, 1.5 equiv), alkene **1a** (0.3 mmol, 3 equiv) and TFE (0.1 M, 1 mL) were added under nitrogen atmosphere. The reaction mixture was stirred (750 rpm) in a preheated aluminum block at 130 °C. After completion of the reaction (monitored by TLC), the solvent was evaporated under reduced pressure, and the crude was purified by column chromatography using EtOAc/hexane as eluent to get the corresponding alkenylated product **3aa/7aa/8aa/9aa**.

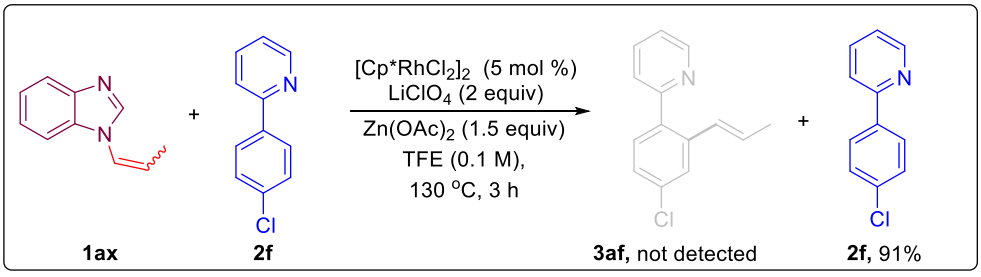
(3.2) General reaction procedure for Rh-catalyzed alkenylation reaction in 1 mmol scale:



To an oven-dried 25 mL Schlenk tube charged with a magnetic stir bar, $LiClO_4$ (2.0 mmol, 2 equiv) was added and heated under reduced pressure to avoid moisture. To this tube, phenyl pyridine **2a** (1 mmol, 1 equiv), $[Cp^*RhCl_2]_2$ (0.05 mmol, 5 mol %), $Zn(OAc)_2$ (1.5 mmol, 1.5 equiv), alkene **1a** (3.0 mmol, 3 equiv) and TFE (0.1 M, 10 mL) were added under nitrogen atmosphere. The reaction mixture was stirred (750 rpm) in a preheated aluminum block at 130 °C. After completion of the reaction (monitored by TLC), the solvent was evaporated under reduced pressure, and the crude was purified by column chromatography using EtOAc/hexane as eluent to get the corresponding alkenylated product **3aa** (144 mg) in 74% yield.

(4) Control and Mechanistic Experiments:

(4.1) General reaction procedure for the standard reaction with internal alkene 1ax:

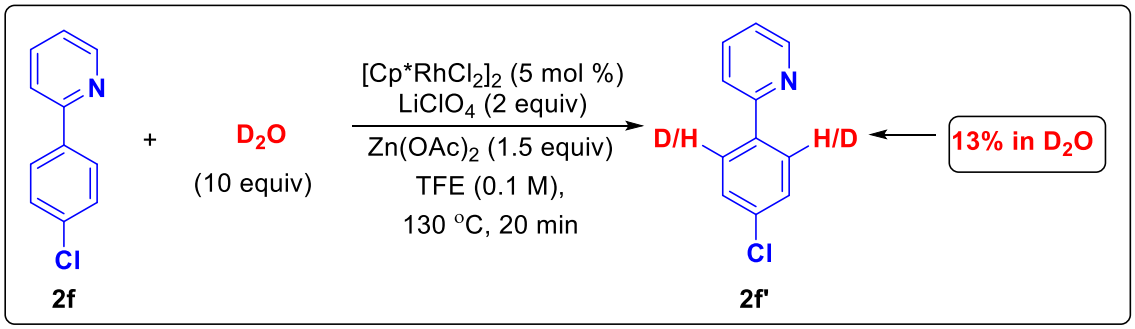


To an oven-dried 25 mL Schlenk tube charged with a magnetic stir bar, $LiClO_4$ (0.2 mmol, 2 equiv) was added and heated under reduced pressure to eliminate a trace of moisture. To this tube, 4-Cl-phenyl pyridine **2f** (0.1 mmol, 1 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 5 mol %), $Zn(OAc)_2$ (0.15 mmol, 1.5 equiv), alkene **1ax** (0.3 mmol, 3 equiv) and TFE (0.1 M, 1 mL) were added under nitrogen atmosphere. The reaction mixture was stirred (750 rpm) in a preheated aluminum block at 130 °C for 3 h. The solvent was evaporated under reduced pressure, and the crude was purified by column

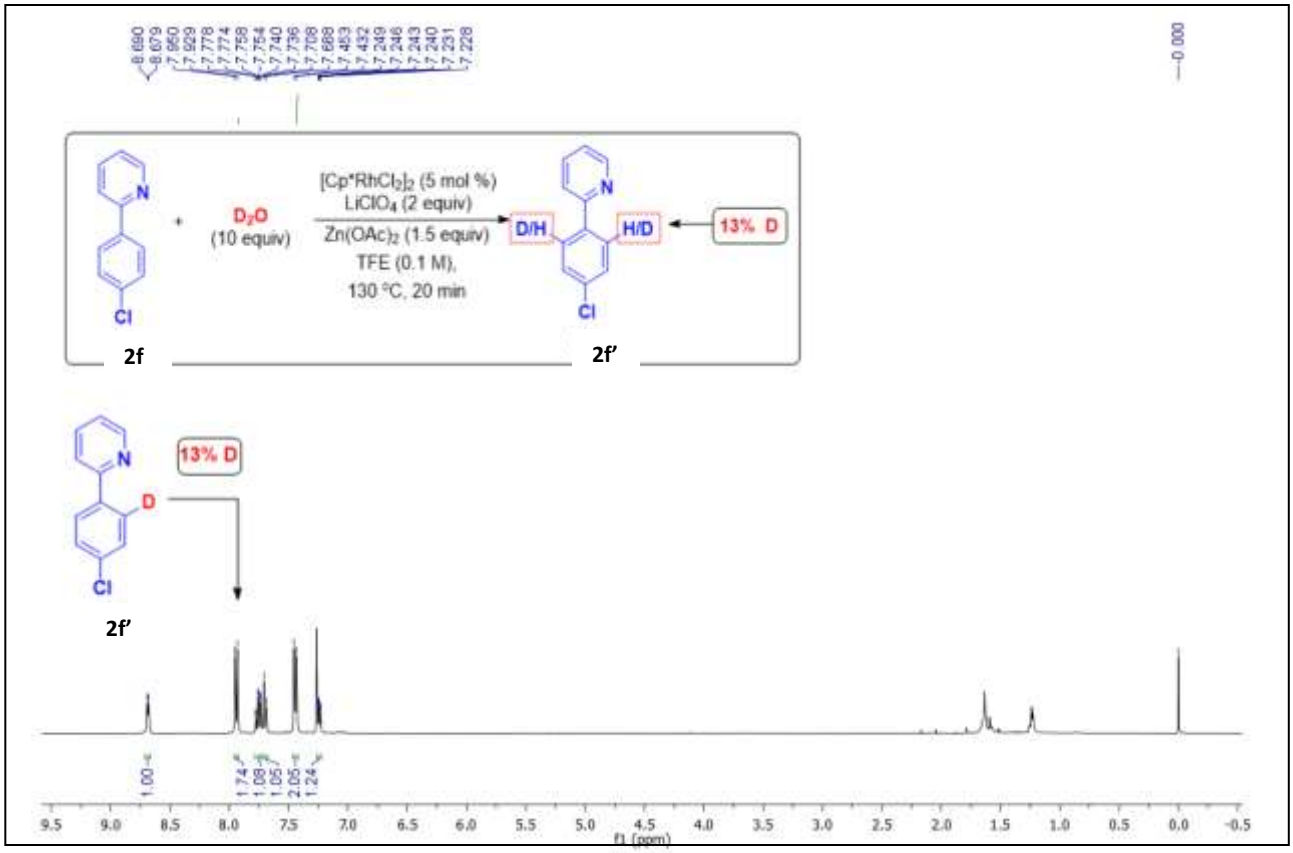
chromatography using EtOAc/hexane as eluent. The starting material **2f** was recovered (17 mg) in 91% yield.

Conclusion: Internal alkene 1ax is not an active coupling partner during the course of the reaction.

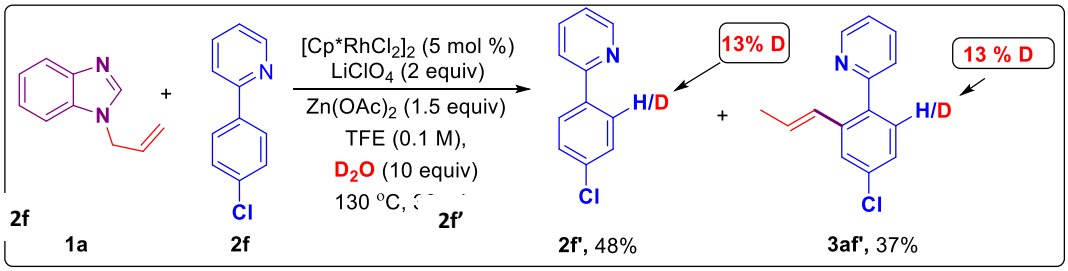
(4.2) H/D scrambling studies with CD_3OD/D_2O:



To an oven-dried 25 mL Schlenk tube charged with a magnetic stir bar, $LiClO_4$ (0.2 mmol, 2 equiv) was added and heated under reduced pressure to eliminate a trace of moisture. To this tube, 4-Cl-phenyl pyridine **2f** (0.1 mmol, 1 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 5 mol %), $Zn(OAc)_2$ (0.15 mmol, 1.5 equiv), CD_3OD/ D_2O (10 equiv) and TFE (0.1 M, 1 mL) were added under nitrogen atmosphere. The reaction mixture was stirred (750 rpm) in a preheated aluminum block at 130 °C for 20 min. The solvent was evaporated under reduced pressure. The percentage of deuterium incorporation was calculated form the crude ^{1}H-NMR spectrum.



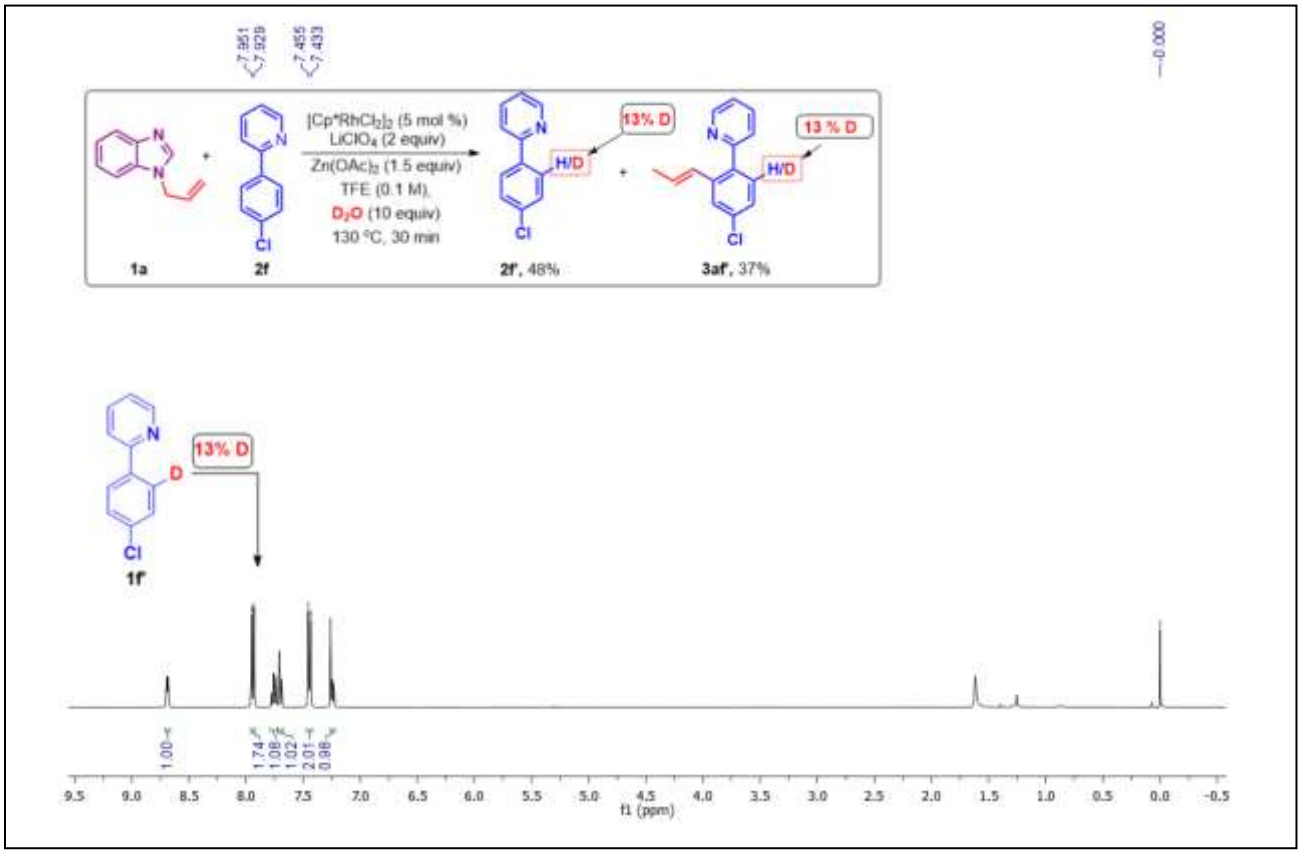
(4.3) H/D scrambling studies with D_2O in presence of alkene:

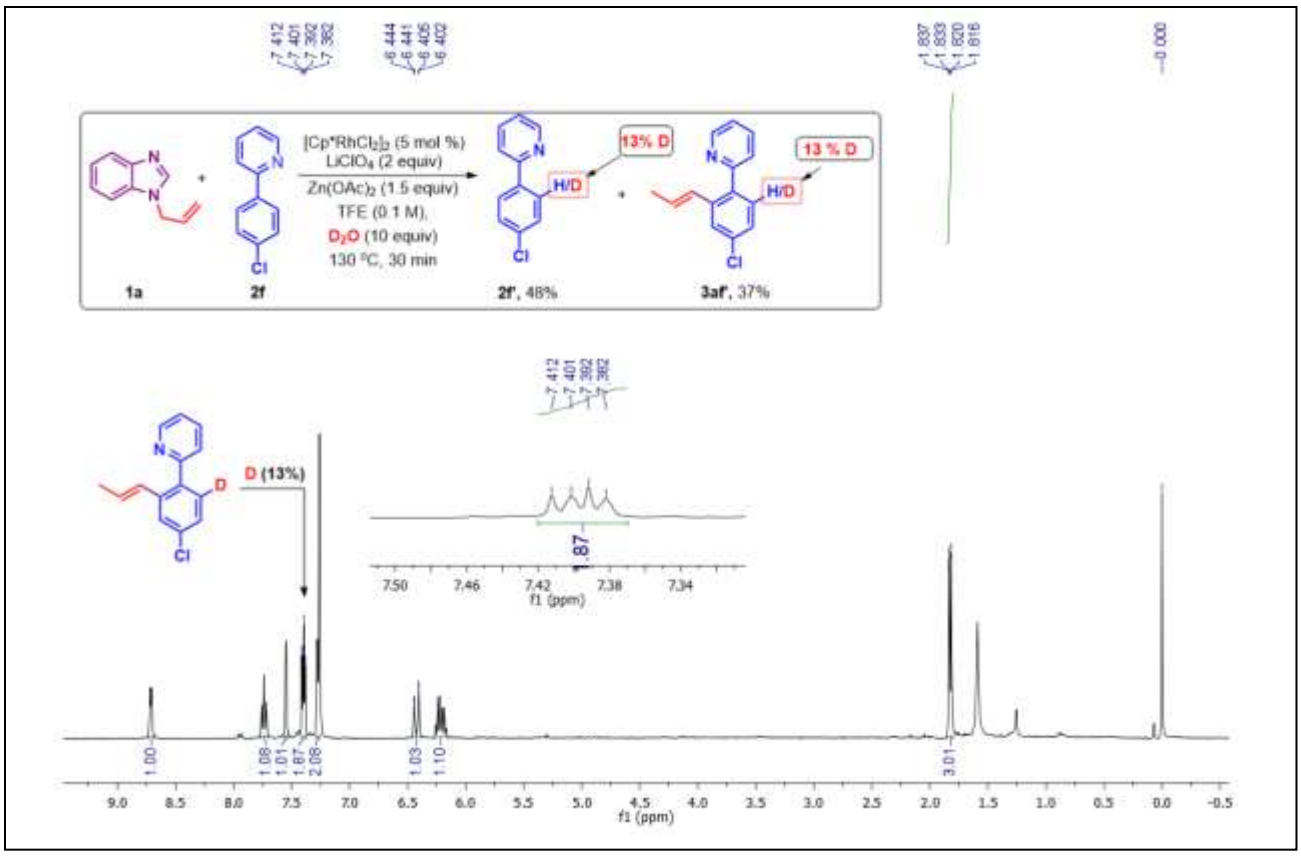


To an oven-dried 25 mL Schlenk tube charged with a magnetic stir bar, $LiClO_4$ (0.2 mmol, 2 equiv) was added and heated under reduced pressure to eliminate a trace of moisture. To this tube, 4-chlorophenylpyridine **2f** (0.1 mmol, 1 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 5 mol %), $Zn(OAc)_2$ (0.15 mmol, **2f'** quiv), alkene **1a** (0.3 mmol, 3 equiv), D_2O (1 mmol, 10 equiv) and TFE (0.1 M, 1 mL) were added under nitrogen atmosphere. The reaction mixture was stirred (750 rpm) in a preheated aluminum block at 130 °C for 30 min. The solvent was evaporated under reduced pressure and was purified by column chromatography using EtOAc/hexane as eluent giving **2f'** (9 mg) and **3af'** (8 mg)

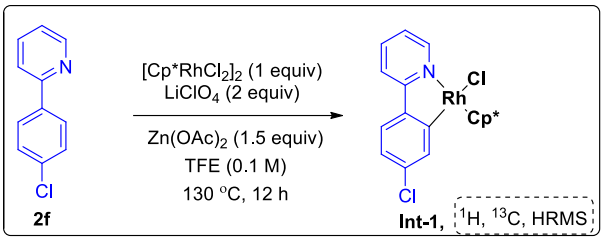
in 48% and 37% yield respectively. The percentage of deuterium incorporation was calculated from ^{1}H-NMR spectrum of isolated **2f'** and **3af'**.

Conclusion: Cyclometalation step is reversible.



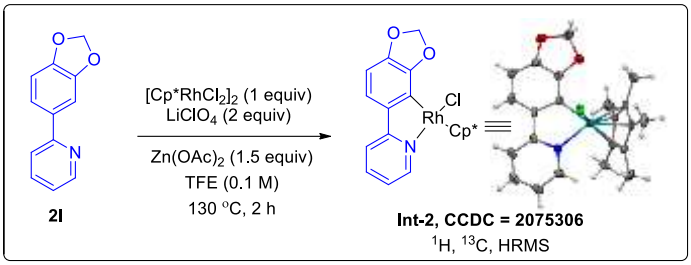


(4.4) Synthesis of Intermediate-1 (Int-1):



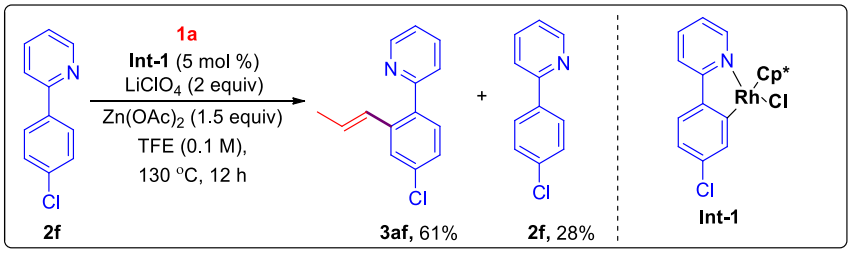
To an oven-dried 25 mL Schlenk tube charged with a magnetic stir bar, $LiClO_4$ (0.1 mmol, 2 equiv) was added and heated under reduced pressure to eliminate a trace of moisture. To this tube, 4-chlorophenylpyridine **2f** (0.05 mmol, 1 equiv), $[Cp^*RhCl_2]_2$ (0.05 mmol, 1 equiv), $Zn(OAc)_2$ (0.075 mmol, 1.5 equiv) and TFE (0.1 M, 0.5 mL) were added under nitrogen atmosphere. The reaction mixture was stirred (750 rpm) in a preheated aluminum block at 130 °C for 12 h. The solvent was removed under reduced pressure and was recrystallized with methanol/DCM. The reddish-colored crystals obtained (17 mg) in 73% yield were characterized by NMR and HRMS.

(4.5) Synthesis of Intermediate-2 (Int-2):



To an oven-dried 25 mL Schlenk tube charged with a magnetic stir bar, $LiClO_4$ (0.1 mmol, 2 equiv) was added and heated under reduced pressure to avoid moisture. To this tube, 2-(benzo[*d*][1,3]dioxol-5-yl)pyridine **2l** (0.05 mmol, 1 equiv), $[Cp^*RhCl_2]_2$ (0.05 mmol, 1 equiv), $Zn(OAc)_2$ (0.075 mmol, 1.5 equiv) and TFE (0.1 M, 0.5 mL) were added under nitrogen atmosphere. The reaction mixture was stirred (750 rpm) in a preheated aluminum block at 130 °C for 2 h. The solvent was removed under reduced pressure and was recrystallized from methanol/DCM. The reddish-colored crystals obtained (12 mg) in 50% yield were characterized by NMR, HRMS, and single crystal X-ray.

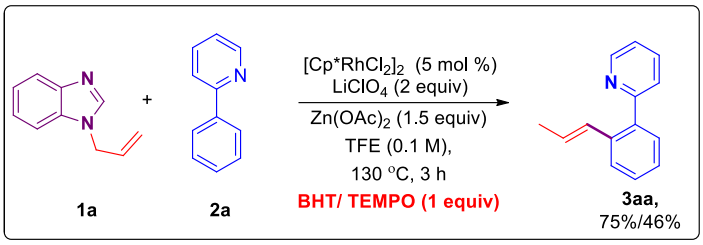
(4.6) General procedure of the standard reaction with Intermediate-1(Int-1):



To an oven dried 25 mL Schlenk tube charged with a magnetic stir bar, $LiClO_4$ (0.2 mmol, 2 equiv) was added and heated under reduced pressure to eliminate trace of moisture. To this tube, 4-Cl-phenyl pyridine **2f** (0.1 mmol, 1 equiv), **Int-1** (0.005 mmol, 5 mol %), $Zn(OAc)_2$ (0.15 mmol, 1.5 equiv), alkene **1a** (0.3 mmol, 3 equiv), and TFE (0.1 M, 1 mL) were added under nitrogen atmosphere. The reaction mixture was stirred (750 rpm) in a preheated aluminum block at 130 °C. The reaction was monitored by TLC. After 12 h, the solvent was evaporated under reduced pressure, and the crude mixture was purified by column chromatography using EtOAc/hexane as eluent giving **3af** (15 mg), **2f** (5 mg) in 61% and 28% yield respectively.

Conclusion: Int-1 is involved as an active Rhoda-cycle intermediate during the reaction.

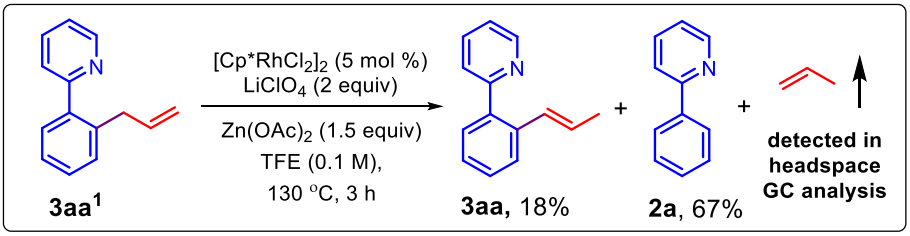
(4.7) Standard reaction with radical scavenger TEMPO or BHT:



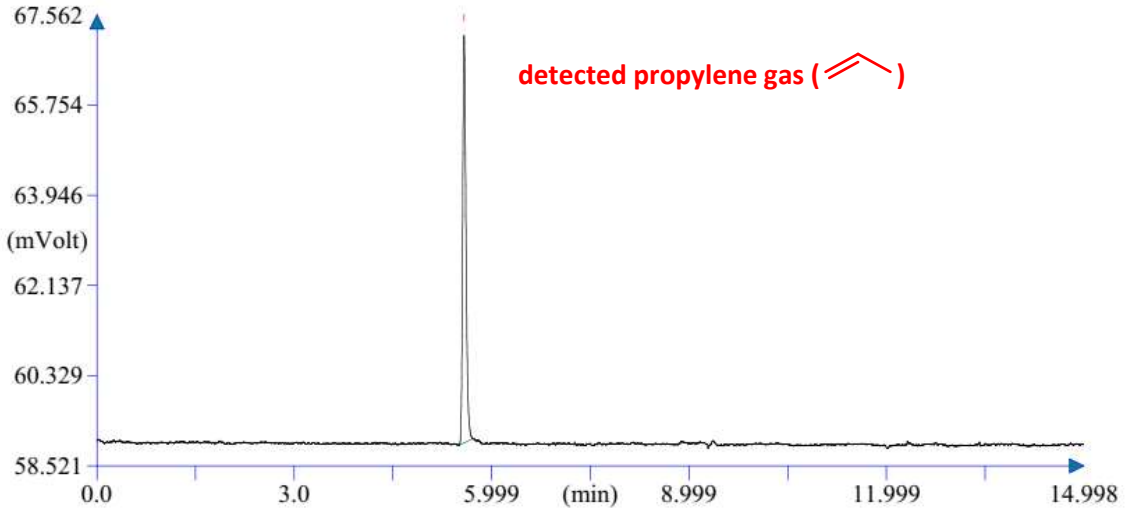
To an oven-dried 25 mL Schlenk tube charged with a magnetic stir bar, $LiClO_4$ (0.2 mmol, 2 equiv) was added and heated under reduced pressure to eliminate a trace of moisture. To this tube, phenyl pyridine **2a** (0.1 mmol, 1 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 5 mol %), $Zn(OAc)_2$ (0.15 mmol, 1.5 equiv), alkene **1a** (0.3 mmol, 3 equiv), BHT/TEMPO (0.1 mmol, 1 equiv), and TFE (0.1 M, 1 mL) were added under nitrogen atmosphere. The reaction mixture was stirred (750 rpm) in a preheated aluminum block at 130 ℃ for 3 h. The reaction was monitored by TLC. The solvent was evaporated under reduced pressure, and the crude mixture was purified by column chromatography using EtOAc/hexane as eluent, which afforded the corresponding alkenylated product **3aa** (15 mg/9 mg) in 75%/46% yield from BHT and TEMPO experiment respectively.

Conclusions: The reaction is not going through a radical mechanism.

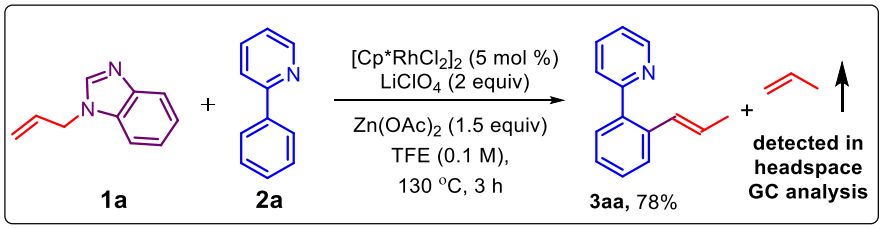
(4.8) Detection of propylene gas through head-space GC analysis:



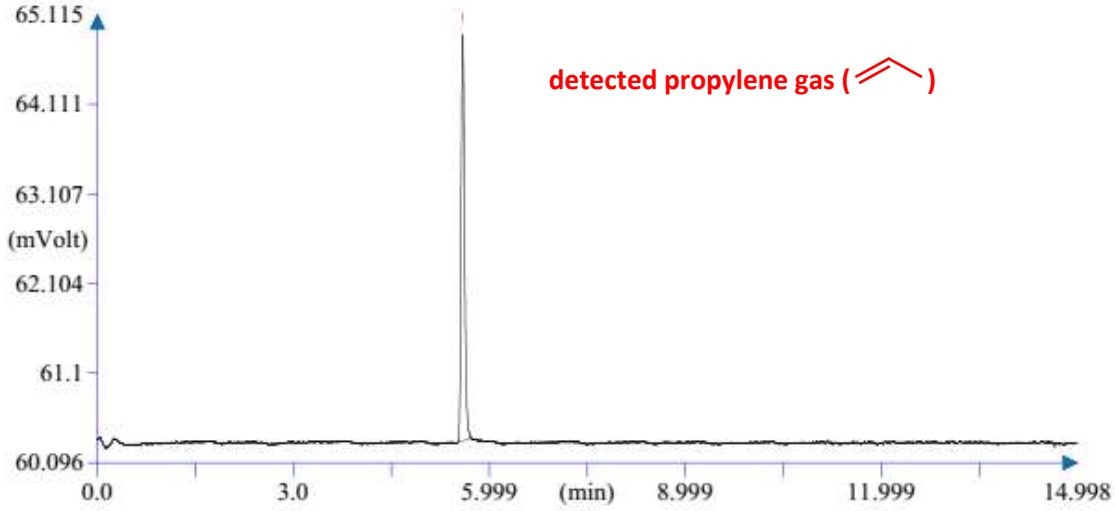
To an oven-dried 25 mL, Schlenk tube charged with a magnetic stir bar was added $LiClO_4$ (0.2 mmol, 2 equiv) and heated under reduced pressure. To this tube, 2'-allyl phenyl pyridine **3aax** (0.1 mmol, 1 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 5 mol %), $Zn(OAc)_2$ (0.15 mmol, 1.5 equiv) followed by TFE (0.1 M, 1 mL) were added under nitrogen atmosphere. The reaction mixture was stirred (750 rpm) in a preheated aluminum block at 130 ℃ for 3 h. Then the gas was collected from the reaction tube through the side arm by a gas trap syringe and was injected into the gas chromatography.



Peak Number (#)	Retention Time (min)	Area (.1*uV*sec)	Area % (%)	Original
1	5.580	285108	100.000	0.000



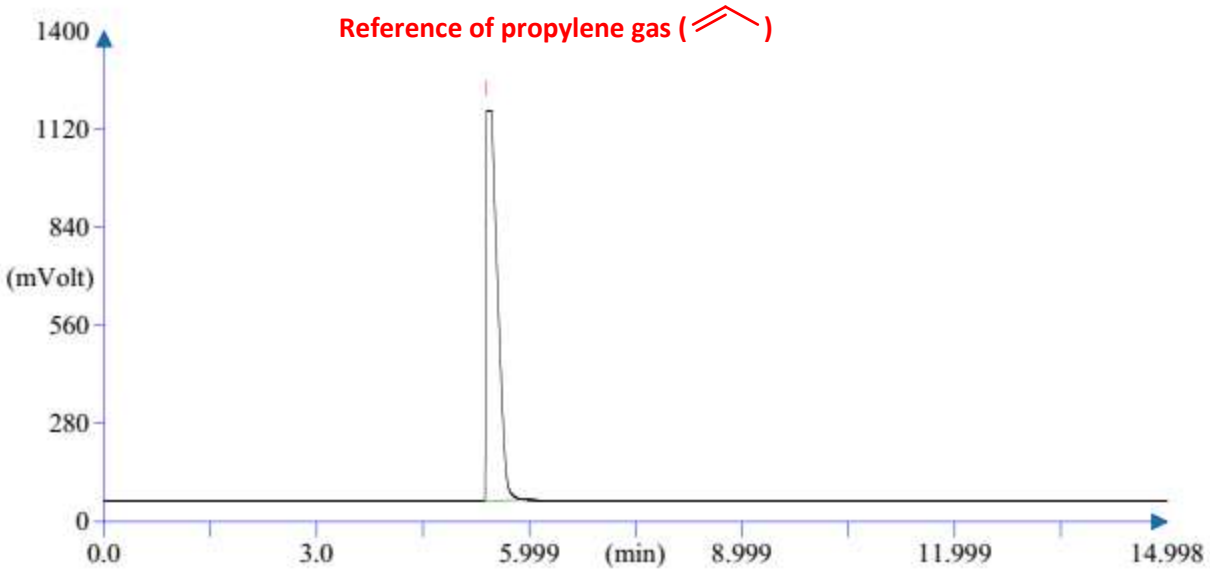
To an oven-dried 25 mL Schlenk tube charged with a magnetic stir bar, was added $LiClO_4$ (0.2 mmol, 2 equiv) and heated under reduced pressure. To this tube, phenylpyridine **2a** (0.1 mmol, 1 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 5 mol %), $Zn(OAc)_2$ (0.15 mmol, 1.5 equiv), alkene **1a** (0.3 mmol, 3 equiv) followed by TFE (0.1 M, 1 mL) were added under nitrogen atmosphere. The reaction mixture was stirred (750 rpm) in a preheated aluminum block at 130 °C for 3 h. Then the gas was collected from the reaction tube through the side arm by a gas trap syringe and was injected into the GC.



detected propylene gas ( )

Peak Number (#)	Retention Time (min)	Area (.1*uV*sec)	Area % (%)	Original
1	5.592	161456	100.000	0.000

Operator ID:	TANMAY
Company name:	Lab
Method filename:	D:\FID - Ranjit April 2022\Cap fid.mth
Method name:	TCD
Analysed:	21-05-2022 17:01
Printed:	21-05-2022 18:25
GC method:	
Sampler method:	
Sample ID:	test77
Channel:	(Channel A)
Analysis type:	UnkNown
Calculation method:	External STD (Area)
Chromatogram filename:	D:\FID - Ranjit April 2022\test77.dat
Calibration method:	Response Factors'
Sample amount:	1

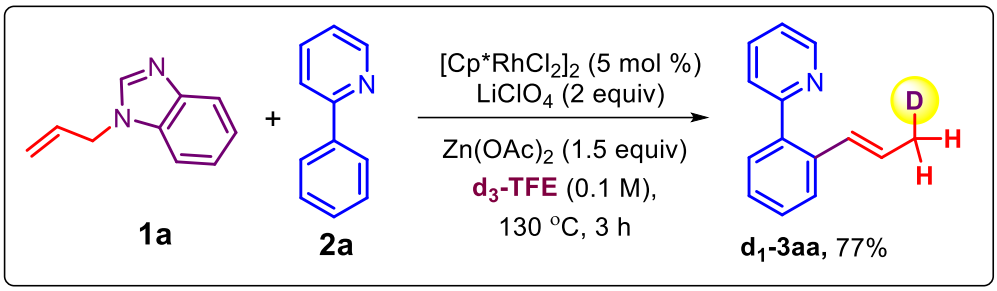


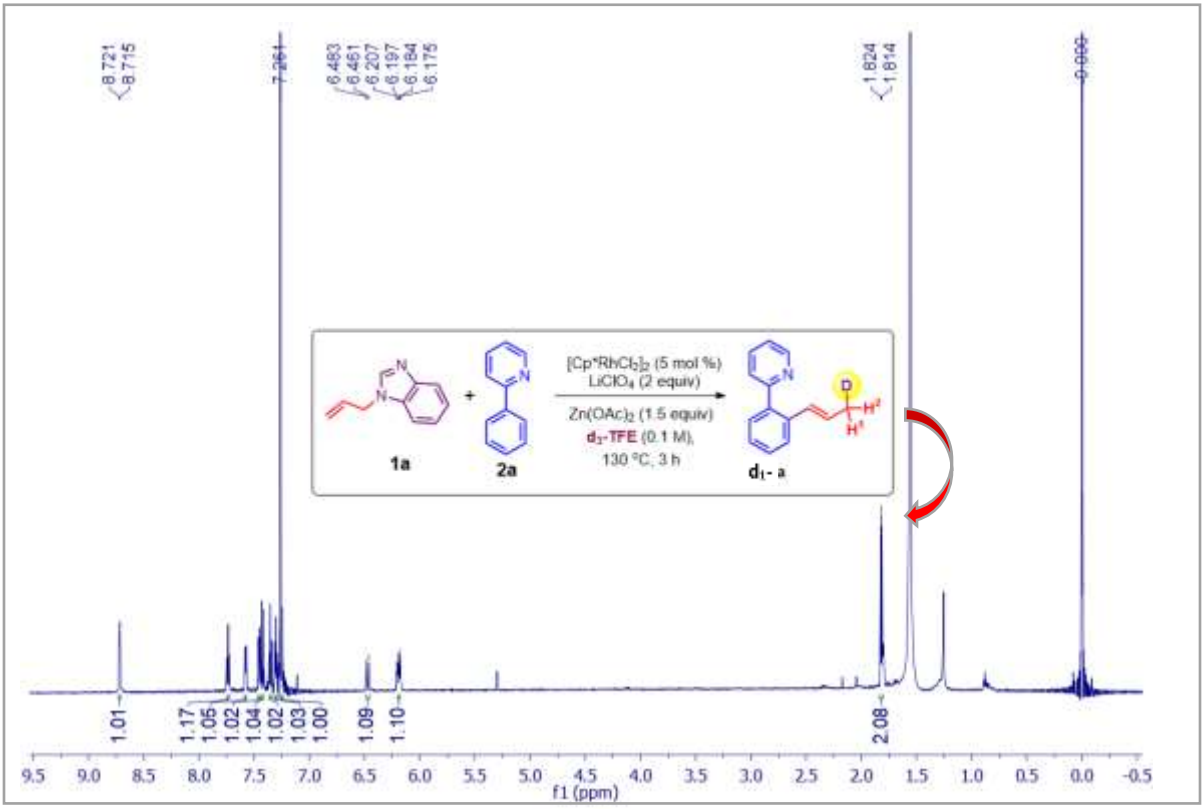
Peak Number (#)	Retention Time (min)	Area (.1*uV*sec)	Area % (%)
1	5.397	123170900	100.000

(4.9) Standard reaction with *d*$_3$-TFE solvent:

To an oven-dried 25 mL Schlenk tube charged with a magnetic stir bar, $LiClO_4$ (0.2 mmol, 2 equiv) was added and heated under reduced pressure to eliminate trace of moisture. To this tube, phenylpyridine **2a** (0.1 mmol, 1 equiv), $[Cp^*RhCl_2]_2$ (0.005 mmol, 5 mol %), $Zn(OAc)_2$ (0.15 mmol,

1.5 equiv), alkene **1a** (0.3 mmol, 3 equiv) followed by d_3-TFE (0.1 M, 1 mL) were added under nitrogen atmosphere. The reaction mixture was stirred (750 rpm) in a preheated aluminum block at 130 °C for 3 h. The reaction was monitored by TLC. The solvent was evaporated under reduced pressure, and the crude mixture was purified by column chromatography using EtOAc/hexane as eluent, which afforded the corresponding alkenylated product **d_1-3aa** (15 mg) in 77% yield.

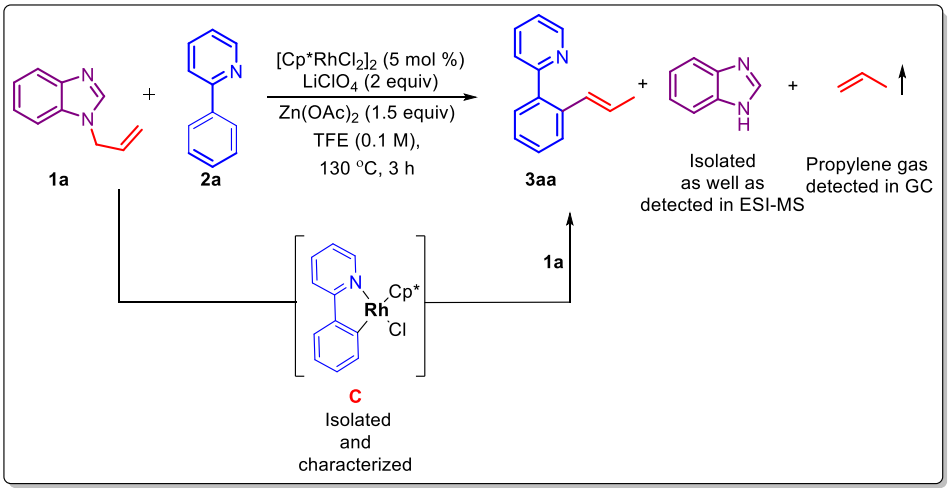


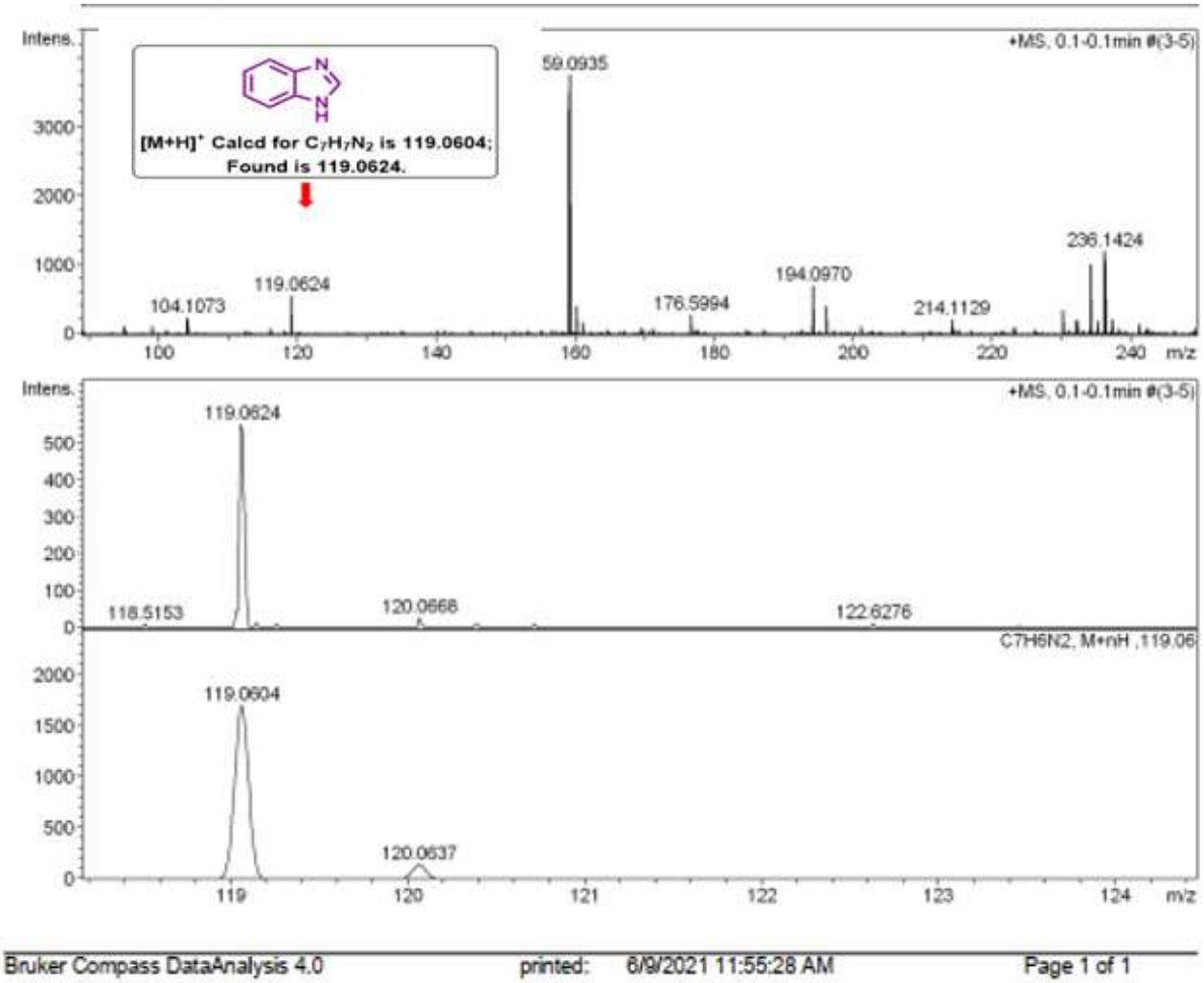


Conclusion: Rh-D is forming in situ, which is the active catalyst for alkene isomerization.[9]

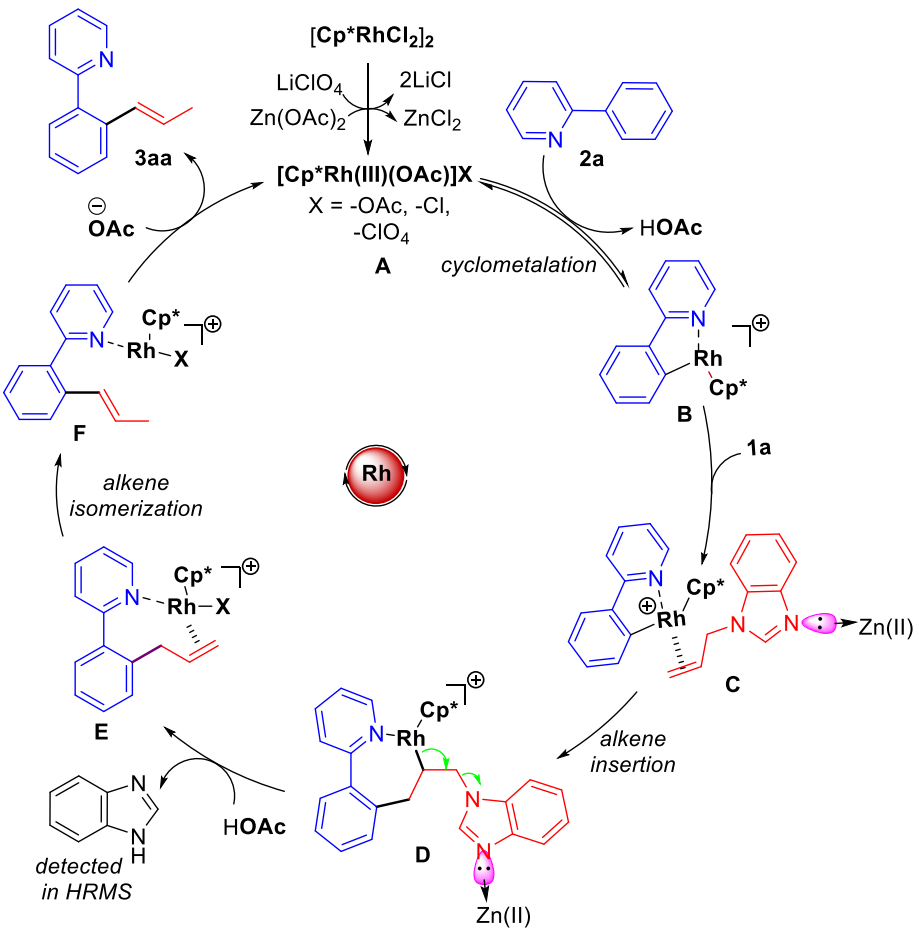
(4.10) Detection of reaction byproducts (HRMS):

The standard reaction was performed, and the reaction mixture was passed through a short celite pad. The crude mixture was submitted for the detection of intermediates and byproducts.

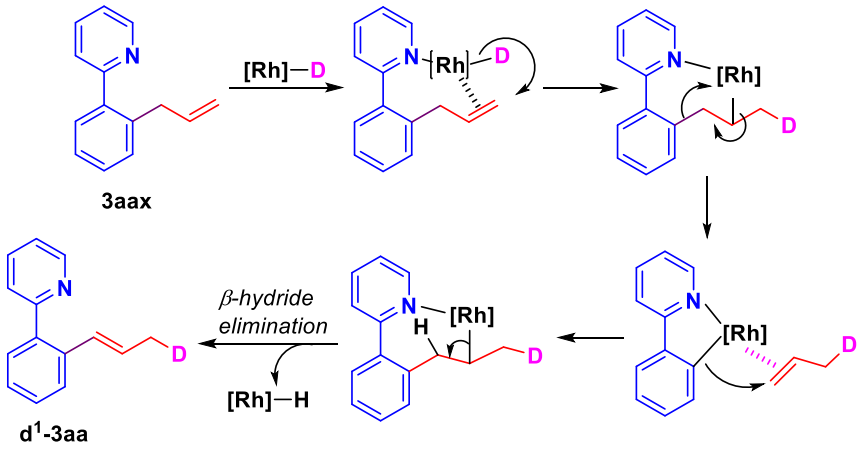

[Cp*RhCl2]2 (5 mol %)
LiClO4 (2 equiv)
Zn(OAc)2 (1.5 equiv)
TFE (0.1 M),
130 °C, 3 h
1a
2a
3aa
Isolated as well as detected in ESI-MS
Propylene gas detected in GC
1a
Cp*
Rh
Cl
C
Isolated and characterized


Intens.
+MS, 0.1-0.1min #(3-5)
[M+H]+ Calcd for C7H7N2 is 119.0604;
Found is 119.0624.
59.0935
236.1424
194.0970
119.0624
104.1073
176.5994
214.1129
m/z
Intens.
+MS, 0.1-0.1min #(3-5)
119.0624
118.5153
120.0668
122.6276
C7H6N2, M+nH ,119.06
119.0604
120.0637
m/z
Bruker Compass DataAnalysis 4.0
printed: 6/9/2021 11:55:28 AM
Page 1 of 1

(4.11) Proposed catalytic cycle:



Detail mechanistic cycle for alkene isomerization step:



Based on our mechanistic investigations and previous literature reports,[10, 11] a catalytic cycle is proposed. The Rh(III) catalyst **A** initially undergoes cyclometalation with **2a** reversibly forming intermediate **B** (characterized by NMR, HRMS, and XRD). π-Complexation of intermediate **B** with

1a, followed by alkene insertion into the C-Rh bond gives intermediate D. The elimination of benzimidazole (detected in HRMS) by the assistance of the zinc additive leads to the allylated intermediate E, which, upon isomerization, delivers the alkenylated product **3aa**.

5. References:

[1] Biswal, P.; Banjare, S. K.; Pati, B. V.; Mohanty, S. R.; Ravikumar, P. C. *J. Org. Chem.* **2021**, *86*, 1108–1117.

[2] Gottlieb, H. E.; Kotlyar, V.; Abraham, N. *J. Org. Chem.* **1997**, *62*, 7512−7515.

[3] L. Hoang, Z Yang, M. Smith, R Pal, L. Miska, E. Pérez, W. Pelter, X. Cheng Z, M. Takacs, *Org. Lett.***2015**, *17*, 940-943.

[4] Ramachandran, K.; Anbarasan, P. *Eur. J. Org. Chem.* **2017**, *2017*, 3965–3968.

[5] Kim, J. Y.; Park, S. H.; Ryu, J.; Hwan, S. C.; Kim, S. H.; Chang, S. *J. Am. Chem. Soc.* **2012**, *134*, 9110–9113.

[6] Zheng, X.; Song, B.; Xu, B. *Eur. J. Org. Chem.* **2010**, *2010*, 4376-4380.

[7] Németh, J.; Debreczeni, N.; Gresits, I. *Catal Lett.* **2015**, *145*, 1113–1119.

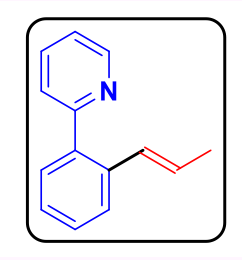
[8] Brændvang, M.; Gundersen, L.-L *Bioorg. Med. Chem.* **2005**, *13*, 6360-6373.

[9] Syntheses of Cp*Rh-hydride complexes by reaction with alcohol solvents: a) White, C.; Oliver, A. J.; Maitlis, P. M. J. Chem. Soc., Dalton Trans. **1973**, 1901. (b) Nutton, A.; Bailey, P. M.; Maitlis, P. M. *J. Organomet. Chem.* **1981**, *213*, 313. A Cp*Rh-hydride complex, which is formed by oxidation alcohol, is considered to be an active species in the α-methylation of ketones and functionalization of styrene via C-C bond cleavage: (c) Chan, L. K. M.; Poole, D. L.; Shen, D.; Healy, M. P.; Donohoe, T. J. *Angew. Chem., Int. Ed*. **2014**, *53*, 761 (d) Onodera, S.; Togashi, R.; Ishikawa, S.; Kochi, T.; Kakiuchi, F. *J. Am. Chem. Soc.* **2020**, *142*, 7345.

[10] (a) Yan, R.; Wang, Z. X. *Org. Biomol. Chem*. **2018**, *16*, 3961; b) Hu, X.-Q.; Hu, Z.; Zhang, G.; Sivendran, N.; Gooßen, L. J. *Org. Lett*. **2018**, *20*, 4337.

[11] Selected reports on Rh-catalyzed alkene isomerization: a) Tsang, D. S.; Yang, S.; Alphonse, F.-A.; Yudin, A. K. *Chem. - Eur. J.* **2008**, *14*, 886. b) Hassam, M.; Taher, A.; Arnott, G. E.; Green, I. R.; van Otterlo, W. A. L. *Chem. Rev*. **2015**, *115*, 5462. c) Azpíroz, R.; Di Giuseppe, A.; Urriolabeitia, A.; Passarelli, V.; Polo, V.; Pérez-Torrente, J. J.; Oro, L. A.; Castarlenas, R. *ACS Catal*. **2019**, *9*, 9372. d) Massad, I.; Marek, I. *ACS Catal.* **2020**, *10*, 5793. e) Fiorito, D.; Scaringi, S.; Mazet, C. *Chem. Soc. Rev*. **2021**, *50*, 1391.

6. Experimental characterization data of products:



(*E*)-*2-(2-(Prop-1-en-1-yl)phenyl)pyridine* (3aa): was prepared according to the general procedure **3.1** (3 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3aa** (16 mg) in 82% yield.

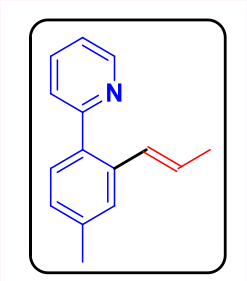
Physical State: colorless liquid
R_f-value: 0.5 (10% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.64 (d, *J* = 4.8 Hz, 1H), 7.65 (dt, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.38 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.30-7.16 (m, 3H), 6.40 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H), 6.16-6.07 (m, 1H), 1.74 (dd, *J* = 6.4 Hz, 1.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 159.5, 149.7, 139.0, 136.5, 136.1, 130.3, 129.8, 128.7, 127.5, 127.1, 126.4, 125.2, 121.9, 19.0.

IR (KBr, cm^{-1}): 3414, 2912, 1584, 1424, 964.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}N$ 196.1121; Found 196.1127.



***(E)-2-(4-Methyl-2-(prop-1-en-1-yl)phenyl)pyridine* (3ab)**: was prepared according to the general procedure **3.1** (3 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3ab** (16 mg) in 77% yield.

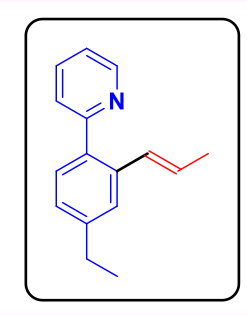
Physical State: colorless liquid
R_f-value: 0.3 (10% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70 (d, *J* = 4.4 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.41-7.35 (m, 3H), 7.24-7.20 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.22-6.13 (m, 1H), 2.39 (s, 3H), 1.81 (d, *J* = 6.4 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 159.5, 149.6, 138.4, 136.3 (2C), 136.1, 130.3, 129.9, 128.0, 127.2, 127.1, 125.2, 121.7, 21.6, 19.0.

IR (KBr, cm^{-1}): 3458, 2913, 1608, 1585, 1464, 964.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{16}N$ 210.1277; Found 210.1284.



(E)-2-(4-Ethyl-2-(prop-1-en-1-yl)phenyl)pyridine **(3ac)**: was prepared according to general procedure **3.1** (4 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3ac** (14 mg) in 63% yield.

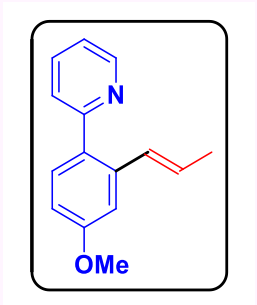
Physical State: Oily liquid
R_f-value: 0.4 (5% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70 (m, 1H), 7.71 (td, J = 7.6 Hz, 2.0 Hz, 1H), 7.42-7.38 (m, 3H), 7.24-7.21 (m, 1H), 7.15 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 6.48 (dd, J = 15.6 Hz, 1.6 Hz, 1H), 6.23-6.14 (m, 1H), 2.69 (q, J = 7.6 Hz, 2H), 1.82 (dd, J = 6.8 Hz, 1.6 Hz, 3H), 1.27 (t, J = 7.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 159.5, 149.6, 144.8, 136.5, 136.3, 136.1, 130.3, 130.0, 127.2, 126.9, 125.9, 125.2, 121.7, 29.1, 19.0, 15.9.

IR (KBr, cm^{-1}): 3499, 2962, 1607, 1585, 1463, 965.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}N$ 224.1434; Found 224.1453.



(E)-2-(4-Methoxy-2-(prop-1-en-1-yl)phenyl)pyridine **(3ad)**: was prepared according to the general procedure **3.1** (4 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3ad** (17 mg) in 76% yield.

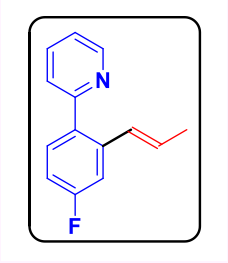
Physical State: colorless liquid
R_f-value: 0.3 (10% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.69 (d, J = 4.0 Hz, 1H), 7.70 (td, J = 7.6 Hz, 1.6 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.22-7.19 (m, 1H), 7.08 (d, J = 2.0 Hz, 1H), 6.86 (dd, J = 8.4 Hz, 2.4 Hz, 1H), 6.49 (dd, J = 15.6 Hz, 1.6 Hz, 1H), 6.23-6.14 (m, 1H), 3.86 (s, 3H), 1.82 (dd, J = 6.4 Hz, 1.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 160.0, 159.2, 149.6, 137.9, 136.1, 132.1, 131.7, 130.0, 127.7, 125.2, 121.5, 113.1, 111.4, 55.6, 19.0.

IR (KBr, cm^{-1}): 3424, 2929, 1602, 1586, 1462, 963.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{16}NO$ 226.1226; Found 226.1230.



(*E*)-*2-(4-Fluoro-2-(prop-1-en-1-yl)phenyl)pyridine* (3ae): was prepared according to general procedure **3.1** (2 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3ae** (17 mg) in 80% yield.

Physical State: colorless liquid
R_f-value: 0.4 (10% EtOAc/hexane)

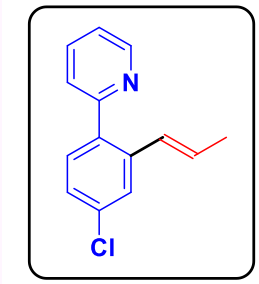
^{1}H NMR ($CDCl_3$, 700 MHz): δ 8.70 (d, J = 4.2 Hz, 1H), 7.73 (td, J = 7.7 Hz, 2.1 Hz, 1H), 7.43 (dd, J = 6.3 Hz, 2.1 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.26-7.24 (m, 2H), 6.99 (td, J = 7.7 Hz, 2.1 Hz, 1H), 6.44 (d, J = 15.4 Hz, 1H) 6.23-6.18 (m, 1H), 1.82 (dd, J = 6.3 Hz, 1.4 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 163.2 (d, J_{C-F} = 244.8 Hz), 158.6, 149.7, 138.7 (d, J_{C-F} = 8.0 Hz), 136.3, 135.1 (d, J_{C-F} = 2.8 Hz), 132.2 (d, J_{C-F} = 8.7 Hz), 129.0 (d, J_{C-F} = 2.1 Hz), 128.8, 125.2, 122.0, 114.1 (d, J_{C-F} = 21.5 Hz), 112.7 (d, J_{C-F} = 22.0), 19.0.

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

IR (KBr, cm^{-1}): 3393, 2912, 1606, 1587, 1463, 1159, 963.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{13}FN$ 214.1027; Found 214.1030.



(*E*)-*2-(4-Chloro-2-(prop-1-en-1-yl)phenyl)pyridine* (3af): was prepared according to the general procedure **3.1** (3 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3af** (17 mg) in 75% yield.

Physical State: Oily liquid
R_f-value: 0.45 (10% EtOAc/hexane)

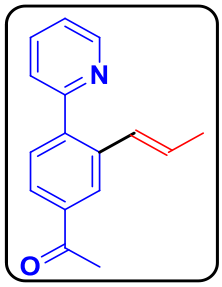
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70 (d, J = 4.4 Hz, 1H), 7.73 (td, J = 7.6 Hz, 1.6 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.41-7.38 (m, 2H), 7.28-7.24 (m, 2H), 6.42 (dd, J = 15.6 Hz, 1.6 Hz, 1H), 6.25-6.16 (m, 1H), 1.82 (dd, J = 6.8 Hz, 1.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 158.4, 149.8, 138.2, 137.3, 136.3, 134.7, 131.7, 128.9, 128.8, 127.1, 126.4, 125.1, 122.2, 19.0.

IR (KBr, cm^{-1}): 3422, 2912, 1592, 1462, 1099, 961.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{13}ClN$ 230.0731; Found 230.0732.

(E)-1-(3-(Prop-1-en-1-yl)-4-(pyridin-2-yl)phenyl)ethanone **(3ag):** was prepared according to general procedure **3.1** (3 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3ag** (19 mg) in 80% yield.



Physical State: colorless liquid
R_f-value: 0.4 (20% EtOAc/hexane)

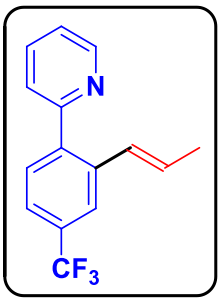
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.74 (d, J = 4.4 Hz, 1H), 8.16 (d, J = 1.6 Hz, 1H), 7.87 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.77 (td, J = 7.6 Hz, 1.6 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.31-7.28 (m, 1H), 6.49 (dd, J = 15.6 Hz, 1.6 Hz, 1H), 6.35-6.26 (m, 1H), 2.65 (s, 3H), 1.85 (dd, J = 6.8 Hz, 1.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 198.4, 158.4, 149.9, 143.1, 137.2, 137.0, 136.4, 130.7, 129.1 (2C), 126.8, 126.7, 125.2, 122.6, 27.1, 19.0.

IR (KBr, cm^{-1}): 3429, 2915, 1683, 1584, 1356, 1240, 964.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}NO$ 238.1226; Found 238.1218.

(E)-2-(2-(prop-1-en-1-yl)-4-(trifluoromethyl)phenyl)pyridine **(3ah):** was prepared according to general procedure **3.1** (2 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3ah** (22 mg) in 84% yield.



Physical State: colorless liquid
R_f-value: 0.5 (10% EtOAc/hexane)

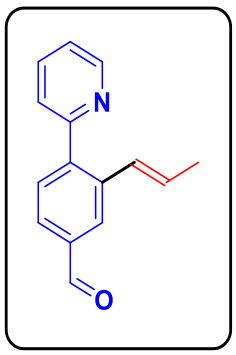
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.74 (d, J = 4.8 Hz, 1H), 7.81 (s, 1H), 7.77 (td, J = 7.6 Hz, 2.0 Hz, 1H), 7.58-7.52 (m, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.32-7.29 (m, 1H), 6.47 (dd, J = 15.6 Hz, 1.6 Hz, 1H), 6.23-6.25 (m, 1H), 1.84 (dd, J = 6.4 Hz, 1.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 158.2, 149.9, 141.9, 137.2, 136.4, 130.8, 129.5, 129.2, 128.7, 127.2 (q, J_{C-F} = 264.0 Hz), 125.1, 123.6 (q, J_{C-F} = 3.7 Hz), 123.4 (q, J_{C-F} = 3.9 Hz), 122.6, 19.0.

^{19}F NMR ($CDCl_3$, 376 MHz): δ -62.6.

IR (KBr, cm^{-1}): 3460, 2915, 1651, 1586, 1336, 1124, 962.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}F_3N$ 264.0995; Found 264.0985.



(*E*)-*3-(Prop-1-en-1-yl)-4-(pyridin-2-yl)benzaldehyde* (3ai): was prepared according to the general procedure **3.1** (5 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3ai** (18 mg) in 81% yield.

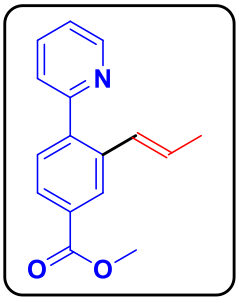
Physical State: Oily liquid
R_f-value: 0.5 (30% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.07 (s, 1H), 8.74 (d, J = 4.0 Hz, 1H), 8.07 (d, J = 1.6 Hz, 1H), 7.81-7.75 (m, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.32-7.29 (m, 1H), 6.59 (dd, J = 15.6 Hz, 1.6 Hz, 1H), 6.36-6.27 (m, 1H), 1.86 (dd, J = 6.8 Hz, 1.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 192.5, 158.3, 150.0, 144.4, 137.6, 136.6, 136.4, 131.2, 129.5, 128.8, 128.2, 127.9, 125.1, 122.7, 19.0.

IR (KBr, cm^{-1}): 3431, 2921, 1695, 1584, 1435, 963.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}NO$ 224.1070; Found 224.1051.



***Methyl* (*E*)-*3-(prop-1-en-1-yl)-4-(pyridin-2-yl)benzoate* (3aj):** was prepared according to general procedure **3.1** (13 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3aj** (20 mg) in 79% yield.

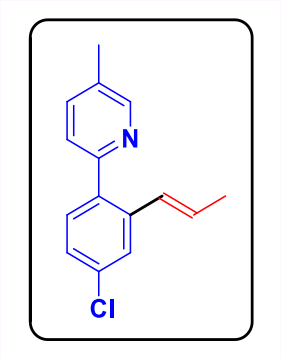
Physical State: Oily liquid
R_f-value: 0.4 (20% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 700 MHz): δ 8.74 (d, J = 4.2 Hz, 1H), 8.25 (s,1H), 7.95 (dd, J = 7.7 Hz, 1.4 Hz, 1H), 7.76 (td, J = 7.7 Hz, 1.4 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.30-7.28 (m, 1H), 6.47 (d, J = 15.4 Hz, 1H), 6.34-6.29 (m, 1H), 3.94 (s, 3H), 1.84 (dd, J = 6.3 Hz, 1.4 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 167.3, 158.5, 149.9, 142.9, 136.8, 136.4, 130.5, 130.3, 128.9, 128.9, 128.0, 127.9, 125.2, 122.5, 52.5, 19.0.

IR (KBr, cm^{-1}): 3430, 2950, 1720, 1584, 1435, 1290, 1107, 965.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}NO_2$ 254.1176; Found 254.1151.



(E)-2-(4-Chloro-2-(prop-1-en-1-yl)phenyl)-5-methylpyridine **(3ak):** was prepared according to general procedure **3.1** (9 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3ak** (19 mg) in 78% yield.

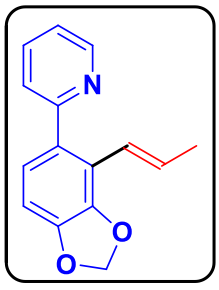
Physical State: Oily liquid
R_f-value: 0.4 (10% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.52 (d, J = 2.0 Hz, 1H), 7.53-7.50 (m, 2H), 7.37 (d, J = 8.4 Hz, 1H), 7.27-7.22 (m, 2H), 6.42 (dd, J = 15.6 Hz, 1.6 Hz, 1H), 6.23-6.14 (m, 1H), 2.40 (s, 3H), 1.83 (dd, J = 6.8 Hz, 1.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 155.5, 150.2, 138.2, 137.3, 136.9, 134.5, 131.7, 131.6, 128.9, 128.7, 127.1, 126.3, 124.6, 19.0, 18.5.

IR (KBr, cm^{-1}): 3413, 2916, 1591, 1469, 1090, 962.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}ClN$ 244.0888; Found 244.0890.



(E)-2-(4-(Prop-1-en-1-yl)benzo[d][1,3]dioxol-5-yl)pyridine **(3al):** was prepared according to general procedure **3.1** (3 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3al** (16 mg) in 67% yield.

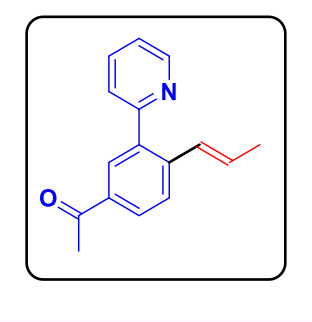
Physical State: colorless liquid
R_f-value: 0.5 (20% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.67 (d, J = 4.0 Hz, 1H), 7.70 (td, J = 7.6 Hz, 1.6 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.24-7.21 (m, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.57-6.48 (m, 1H), 6.25 (dd, J = 16.0 Hz, 1.6 Hz, 1H), 6.04 (s, 2H), 1.81 (dd, J = 6.8 Hz, 1.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 159.3, 149.6, 147.9, 145.6, 136.2, 134.0, 132.0, 125.2, 124.6, 124.2, 121.8, 119.5, 106.8, 101.3, 19.7.

IR (KBr, cm^{-1}): 3413, 2909, 1622, 1585, 1445, 1245, 1059, 943.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}NO_2$ 240.1019; Found 240.1027.



(E)-1-(4-(Prop-1-en-1-yl)-3-(pyridin-2-yl)phenyl)ethan-1-one **(3an):** was prepared according to the general procedure **3.1** (5 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3an** (16 mg) in 67% yield.

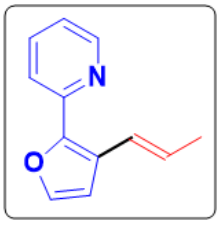
Physical State: Oily liquid
R_f-value: 0.4 (20% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.74 (d, J = 4.4 Hz, 1H), 8.03 (d, J = 2.0 Hz, 1H), 7.95 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.77 (td, J = 7.6 Hz, 1.6 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.32-7.28 (m, 1H), 6.51 (dd, J = 15.6 Hz, 1.2 Hz, 1H), 7.39-7.30 (m, 1H), 2.60 (s, 3H), 1.85 (dd, J = 6.8 Hz, 1.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 197.8, 158.6, 149.8, 141.1, 139.1, 136.5, 135.7, 130.9, 130.4, 129.1, 128.4, 126.6, 125.2, 122.4, 26.9, 19.2.

IR (KBr, cm^{-1}): 3421, 2912, 1680, 1600, 1465, 1241, 964.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}NO$ 238.1226; Found 238.1239.



(E)-2-(3-(prop-1-en-1-yl)furan-2-yl)pyridine **(3ar):** was prepared according to general procedure **3.1** (24 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3ar** (14 mg) in 76% yield.

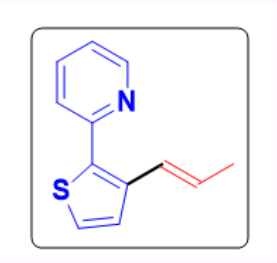
Physical State: Oily liquid
R_f-value: 0.6 (5% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 700 MHz): δ 8.62 (d, J = 4.9 Hz, 1H), 7.70-7.66 (m, 2H), 7.41-7.39 (m, 2H), 7.12-7.10 (m, 1H), 6.67 (d, J = 2.1 Hz, 1H), 6.17-6.11(m, 1H), 1.93 (dd, J = 6.3 Hz, 1.4 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 151.4, 149.6, 147.0, 142.7, 136.6, 128.0, 124.1, 122.8, 121.4, 120.2, 110.3, 19.06.

IR (KBr, cm^{-1}): 3471, 2932, 2911, 1591, 1555, 1445, 973.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}NO$ 186.0913; Found 186.0920.



***(E)-2-(3-(prop-1-en-1-yl)thiophen-2-yl)pyridine* (3as):** was prepared according to the general procedure **3.1** (24 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **3as** (14 mg) in 70% yield.

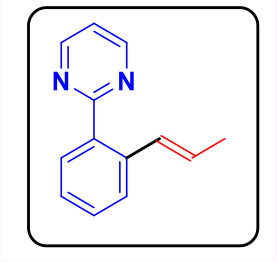
Physical State: Oily liquid
R_f-value: 0.6 (0% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 700 MHz): δ 8.65 (d, J = 4.2 Hz, 1H), 7.71 (td, J = 7.7 Hz, 1.4 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.28 (d, J = 4.9 Hz, 1H), 7.22 (d, J = 5.6 Hz, 1H), 7.18-6.16 (m, 1H), 6.80 (d, J = 15.4 Hz, 1H), 6.24-6.19 (m, 1H), 1.90 (dd, J = 7.0 Hz, 1.4 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 153.5, 150.0, 137.7, 137.6, 136.7, 128.6, 127.5, 126.3, 125.2, 123.1, 121.8, 19.0.

IR (KBr, cm^{-1}): 3470, 2929, 2909, 1581, 1563, 1434, 968.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}NS$ 202.0685; Found 202.0682.



***(E)-2-(2-(Prop-1-en-1-yl)phenyl)pyrimidine* (7aa):** was prepared according to the general procedure **3.1** (20 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **7aa** (13 mg) in 66% yield.

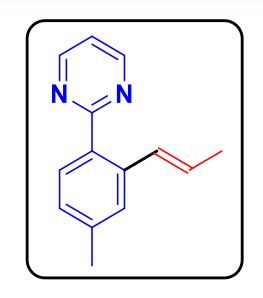
Physical State: colorless liquid
R_f-value: 0.2 (10% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.86 (d, J = 4.8 Hz, 2H), 7.75 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.40 (td, J = 7.6 Hz, 1.2 Hz, 1H), 7.32 (td, J = 7.6 Hz, 1.2 Hz, 1H), 7.25-7.22 (m, 1H), 6.82 (dd, J = 15.6 Hz, 1.2 Hz, 1H), 6.26-6.17 (m, 1H), 1.86 (dd, J = 6.4 Hz, 1.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 167.7, 157.3, 137.3, 136.8, 130.9, 129.9, 129.8, 127.5, 127.1, 126.8, 118.8, 19.1.

IR (KBr, cm^{-1}): 3433, 2912, 1567, 1553, 1414, 961.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}N_2$ 197.1073; Found 197.1080.



(E)-2-(4-Methyl-2-(prop-1-en-1-yl)phenyl)pyrimidine **(7ab)**: was prepared according to the general procedure **3.1** (5 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **7ab** (16 mg) in 76% yield.

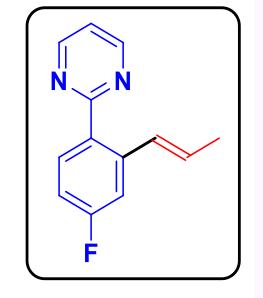
Physical State: colorless liquid
R_f-value: 0.4 (10% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.8 (d, J = 4.8 Hz, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.41 (s, 1H), 7.18 (t, J = 4.8 Hz, 1H), 7.13 (d, J = 7.2 Hz, 1H), 6.89 (dd, J = 15.6 Hz, 1.2 Hz, 1H), 6.22-6.13 (m, 1H), 2.39 (s, 3H), 1.86 (dd, J = 6.4 Hz, 1.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 167.9, 157.1, 139.8, 137.4, 134.3, 131.1, 130.3, 128.0, 127.6, 127.1, 118.6, 21.73, 19.07.

IR (KBr, cm^{-1}): 3032, 2917, 1608, 1566, 1415, 960.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}N_2$ 211.1230; Found 211.1234.



(E)-2-(4-Fluoro-2-(prop-1-en-1-yl)phenyl)pyrimidine **(7ac)**: was prepared according to general procedure **3.1** (11 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **7ac** (19 mg) in 89% yield.

Physical State: colorless liquid
R_f-value: 0.4 (20% EtOAc/hexane)

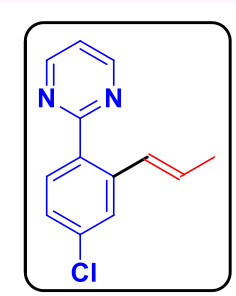
^{1}H NMR ($CDCl_3$, 700 MHz): δ 8.86 (d, J = 4.9 Hz, 2H), 7.79-7.77 (m, 1H), 7.30-7.28 (m, 1H), 7.23 (t, J = 4.9 Hz, 1H), 7.03-7.00 (m, 1H), 6.86 (d, J = 16.1 Hz, 1H), 6.26-6.21 (m, 1H), 1.88-1.86 (m, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 166.9, 163.9 (d, J_{C-F} = 248.1 Hz), 157.3, 140.0 (d, J_{C-F} = 8.2 Hz), 133.3 (d, J_{C-F} = 8.9 Hz), 133.0 (d, J_{C-F} = 2.8 Hz), 129.2 (d, J_{C-F} = 1.9 Hz), 128.8, 118.9, 114.2 (d, J_{C-F} = 21.6 Hz), 113.2 (d, J_{C-F} = 22.3 Hz), 19.1.

^{19}F NMR ($CDCl_3$, 376 MHz): δ -112.0.

IR (KBr, cm^{-1}): 3443, 2912, 1607, 1577, 1409, 1267, 960.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}FN_2$ 215.0979; Found 215.0993.



(*E*)-*2*-*(4*-Chloro-*2*-*(prop*-*1*-*en*-*1*-*yl)phenyl)pyrimidine **(7ad)**: was prepared according to the general procedure **3.1** (20 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **7ad** (19 mg) in 82% yield.

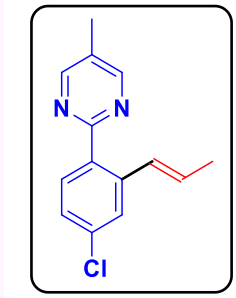
Physical State: colorless liquid
R_f-value: 0.3 (10% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.78 (d, J = 4.8 Hz, 2H), 7.67 (d, J = 8.4 Hz, 1H), 7.51 (s, 1H), 7.23-7.16 (m, 2H), 6.77 (d, J = 15.6 Hz, 1H), 6.21-6.12 (m, 1H), 1.79 (d, J = 6.4 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 166.8, 157.3, 139.2, 136.0, 135.1, 132.5, 129.0, 128.9, 127.1, 126.8, 119.0, 19.1.

IR (KBr, cm^{-1}): 3446, 2923, 1563, 1417, 1265, 1102, 961.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}ClN_2$ 231.0684; Found 231.0678.



(*E*)-*2*-*(4*-Chloro-*2*-*(prop*-*1*-*en*-*1*-*yl)phenyl)*-*5*-*methyl pyrimidine **(7ae):** was prepared according to the general procedure **3.1** (20 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **7ae** (19 mg) in 78% yield.

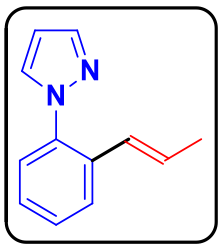
Physical State: colorless liquid
R_f-value: 0.45 (10% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.67 (s, 2H), 7.69 (d, J = 8.4 Hz, 1H), 7.57 (d, J = 2.0 Hz, 1H), 7.27 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 6.82 (dd, J = 15.6 Hz, 1.6 Hz, 1H), 6.27-6.18 (m, 1H), 2.37 (s, 3H), 1.86 (dd, J = 6.4 Hz, 1.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 164.3, 157.5, 139.0, 135.6, 135.2, 132.3, 129.0, 128.7, 128.3, 127.1, 126.7, 19.1, 15.8.

IR (KBr, cm^{-1}): 3452, 2924, 1588, 1429, 1101, 959.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}ClN_2$ 245.0840; Found 245.0843.



(*E*)-*1*-(*2*-(*Prop*-*1*-*en*-*1*-*yl*)*phenyl*)-*1H*-*pyrazole* (8aa): was prepared according to the general procedure **3.1** (3 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **8aa** (12 mg) in 65% yield.

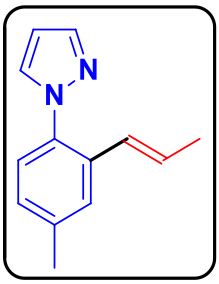
Physical State: colorless liquid
R_f-value: 0.4 (10% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 700 MHz): δ 7.73 (s, 1H), 7.62 (s, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.36-7.34 (m, 2H), 7.29 (td, J = 7.7 Hz, 1.4 Hz, 1H), 6.44 (s, 1H), 6.21-6.20 (m, 2H), 1.82 (d, J = 4.2 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 140.8, 138.3, 133.9, 131.7, 129.0, 128.6, 127.6, 126.9, 126.6, 126.5, 106.6, 19.1.

IR (KBr, cm^{-1}): 3424, 2912, 1691, 1517, 1393, 1044, 965.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{13}N_2$ 185. 1079; Found 185. 1085.



(*E*)-*1*-(*4*-*Methyl*-*2*-(*prop*-*1*-*en*-*1*-*yl*)*phenyl*)-*1H*-*pyrazole* (8ab): was prepared according to the general procedure **3.1** (3 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **8ab** (14 mg) in 70% yield.

Physical State: colorless liquid
R_f-value: 0.4 (5% EtOAc/hexane)

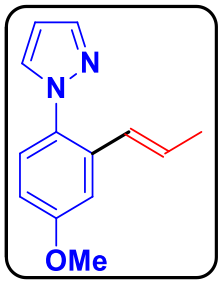
^{1}H NMR ($CDCl_3$, 700 MHz): δ 7.71 (d, J = 1.4 Hz, 1H), 7.57 (d, J = 2.1 Hz, 1H), 7.38 (s, 1H), 7.23 (d, J = 7.7 Hz, 1H), 7.09 (d, J = 7.7 Hz, 1H), 6.42 (t, J = 2.1 Hz, 1H), 6.21-6.17 (m, 1H), 6.15 (d, J = 16.1 Hz, 1H), 2.39 (s, 3H), 1.81 (d, J = 4.9 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 140.6, 138.4, 136.0, 133.6, 131.7, 128.7, 128.4, 127.2, 126.5 (2C), 106.4, 21.5, 19.1.

IR (KBr, cm^{-1}): 3422, 2920, 1690, 1515, 1395, 965.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}N_2$ 199.1230; Found 199.1238.

(*E*)-*1-(4-Methoxy-2-(prop-1-en-1-yl)phenyl)-1H-pyrazole* (8ac): was prepared according to the general procedure **3.1** (3 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **8ac** (17 mg) in 80% yield.



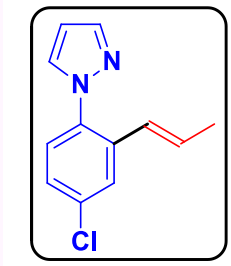
Physical State: colorless liquid
R_f-value: 0.2 (5% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (d, J = 1.6 Hz, 1H), 7.53 (d, J = 2.4 Hz, 1H), 7.25-7.24 (m, 1H), 7.06 (d, J = 2.8 Hz, 1H), 6.82 (dd, J = 8.8 Hz, 3.2 Hz, 1H), 6.41 (t, J = 2.0 Hz, 1H), 6.21-6.14 (m, 1H), 6.09 (dd, J = 15.6 Hz, 1.2 Hz, 1H), 3.85 (s, 3H), 1.80 (dd, J = 6.4 Hz, 1.2 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 159.7, 140.5, 135.5, 131.9, 131.8, 129.2, 128.0, 126.3, 113.2, 111.2, 106.3, 55.8, 19.0.

IR (KBr, cm^{-1}): 3430, 2913, 1652, 1604, 1518, 1294, 1043, 964.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}N_2O$ 215.1179; Found 215.1192.



(*E*)-*1-(4-Chloro-2-(prop-1-en-1-yl)phenyl)-1H-pyrazole* (8ad): was prepared according to the general procedure **3.1** (2 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **8ad** (16 mg) in 73% yield.

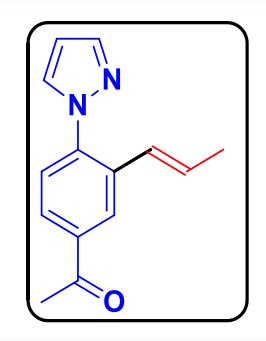
Physical State: colorless liquid
R_f-value: 0.4 (5% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, J = 1.6 Hz, 1H), 7.51 (d, J = 2.0 Hz, 1H), 7.48 (d, J = 2.4 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.19-7.17 (m, 1H), 6.37 (t, J = 2.0 Hz, 1H), 6.21-6.12 (m, 1H), 6.08 (d, J = 16.8 Hz, 1H), 1.76 (d, J = 6.0 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 141.1, 135.4, 134.4, 131.6, 130.5, 127.9, 127.6, 126.8, 125.6, 120.6, 106.9, 19.1.

IR (KBr, cm^{-1}): 3444, 2912, 1651, 1517, 1485, 1109, 955.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{12}ClN_2$ 219.0684; Found 219.0680.



(E)-1-(3-(Prop-1-en-1-yl)-4-(1H-pyrazol-1-yl)phenyl)ethanone **(8ae)**: was prepared according to the general procedure **3.1** (3 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **8ae** (15 mg) in 66% yield.

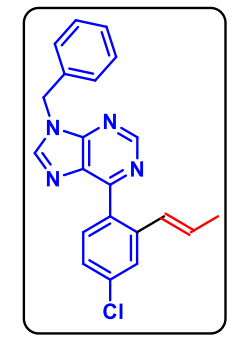
Physical State: colorless liquid
R_f-value: 0.2 (5% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 700 MHz): δ 7.93 (s, 2H), 7.77 (d, J = 1.4 Hz, 1H), 7.68 (d, J = 7.7 Hz, 1H), 7.65 (d, J = 2.1 Hz, 1H), 6.48 (t, J = 2.1 Hz, 1H), 6.39-6.34 (m, 1H), 6.25 (d, J = 16.1 Hz, 1H), 2.60 (s, 3H), 1.87 (dd, J = 6.3 Hz, 1.4 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 197.0, 141.2, 138.4, 138.2, 136.3, 132.0, 131.7, 128.1, 127.0, 125.9, 107.1, 26.9, 19.3.

IR (KBr, cm^{-1}): 3444, 2915, 1682, 1605, 1517, 1450, 1264, 968.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}N_2O$ 227.1179; Found 227.1186.



(E)-9-Benzyl-6-(4-chloro-2-(prop-1-en-1-yl)phenyl)-9H-purine **(9aa)**: was prepared according to the general procedure **3.1** (12 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **9aa** (25 mg) in 70% yield.

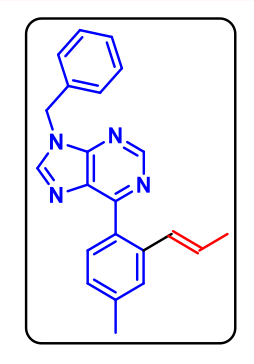
Physical State: colorless liquid
R_f-value: 0.3 (20% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.09 (s, 1H), 8.07 (s, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 2.0 Hz, 1H), 7.41-7.31 (m, 6H), 6.62 (dd, J = 15.6 Hz, 1.6 Hz, 1H), 6.30-6.21 (m, 1H), 5.49 (s, 2H), 1.79 (dd, J = 6.8 Hz, 1.6 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 157.6, 152.7, 152.4, 144.9, 139.3, 136.3, 135.3, 132.9, 132.9, 131.7, 129.5, 129.3, 129.0, 128.4, 128.3, 127.0, 126.6, 47.7, 19.0.

IR (KBr, cm^{-1}): 3435, 2925, 1708, 1580, 1499, 1328, 958.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{18}ClN_4$ 361.1215; Found 361.1222.



(E)-9-Benzyl-6-(4-methyl-2-(prop-1-en-1-yl)phenyl)-9H-purine **(9ab)**: was prepared according to the general procedure **3.1** (12 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **9ab** (26 mg) in 76% yield.

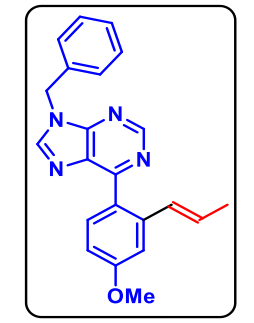
Physical State: Colorless liquid
R_f-value: 0.3 (20% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.07 (s, 1H), 8.02 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.49 (s, 1H), 7.38-7.34 (m, 5H), 7.16 (d, J = 7.6 Hz, 1H), 6.67 (d, J = 15.6 Hz, 1H), 6.24-6.16 (m, 1H), 5.48 (s, 2H), 2.41 (s, 3H), 1.77 (dd, J = 6.8 Hz, 1.2 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 159.1, 152.7, 152.3, 144.5, 140.0, 137.4, 135.6, 132.7, 131.6, 130.8, 129.7, 129.5, 128.9, 128.3, 127.9, 127.4, 127.3, 47.7, 21.8, 19.0.

IR (KBr, cm^{-1}): 3563, 2919, 2851, 1582, 1504, 1454, 963.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}N_4$ 341.1761; Found 341.1773.



(E)-9-benzyl-6-(4-methoxy-2-(prop-1-en-1-yl)phenyl)-9H-purine **(9ac)**: was prepared according to general procedure **3.1** (12 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **9ac** (29 mg) in 81% yield.

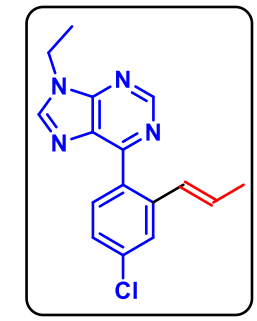
Physical State: Colorless liquid
R_f-value: 0.4 (50% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 700 MHz): δ 9.08 (s, 1H), 8.05 (s, 1H), 7.78 (d, J = 9.1 Hz, 1H), 7.38-7.35 (m, 5H), 7.20 (d, J = 2.1 Hz, 1H), 6.92 (dd, J = 8.4 Hz, 2.8 Hz, 1H), 6.75 (dd, J = 15.4 Hz, 1.4 Hz, 1H), 6.25-6.22 (m, 1H), 5.48 (s, 2H), 3.88 (s, 3H), 1.80 (dd, J = 7.0 Hz, 1.4 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 161.1, 158.6, 152.6, 152.2, 144.4, 139.3, 135.5, 133.4, 132.4, 129.7, 129.5, 128.9, 128.2, 127.9, 126.3, 112.9, 111.9, 55.7, 47.6, 19.0.

IR (KBr, cm^{-1}): 3487, 2934, 2910, 1579, 1504, 1454, 962.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}N_4O$ 357.1710; Found 357.1711.



(E)-6-(4-chloro-2-(prop-1-en-1-yl)phenyl)-9-ethyl-9H-purine **(9ad)**: was prepared according to general procedure **3.1** (12 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **9ad** (20 mg) in 67% yield.

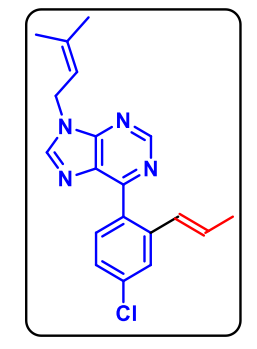
Physical State: Colorless liquid
R_f-value: 0.2 (20% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 700 MHz): δ 9.06 (s, 1H), 8.11 (s, 1H), 7.68-7.67 (m, 2H), 7.33 (dd, *J* = 8.4 Hz, 2.1 Hz, 1H), 6.61 (d, *J* = 15.4 Hz, 1H), 6.29-6.24 (m, 1H), 4.40 (q, *J* = 7.0 Hz, 2H), 1.79 (d, *J* = 6.3 Hz, 3H), 1.63 (d, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 157.5, 152.4, 152.2, 144.6, 139.2, 136.2, 132.9, 132.8, 131.8, 129.2, 128.4, 127.0, 126.6, 39.4, 19.0, 15.7.

IR (KBr, cm^{-1}): 3503, 2935, 2915, 1582, 1501, 1445, 957.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}ClN_4$ 299.1058; Found 299.1061.



(E)-6-(4-chloro-2-(prop-1-en-1-yl)phenyl)-9-(3-methylbut-2-en-1-yl)-9H-purine **(9ae)**: was prepared according to the general procedure **3.1** (12 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **9ae** (24 mg) in 71% yield.

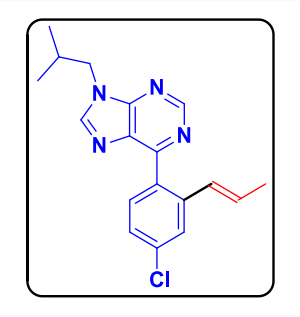
Physical State: Colorless liquid
R_f-value: 0.2 (20% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.06 (s, 1H), 8.07 (s, 1H), 7.68-7.66 (m, 2H), 7.33-7.32 (m, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.30-6.22 (m, 1H), 5.51-5.48 (m, 1H), 4.90 (d, *J* = 3.2 Hz, 2H), 1.88 (s, 3H), 1.83 (s, 3H), 1.79 (d, *J* = 6.8 Hz, 3H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 157.4, 152.4, 152.2, 144.7, 140.2, 139.2, 136.2, 132.9, 132.7, 131.8, 129.2, 128.4, 127.0, 126.6, 117.6, 41.8, 26.0, 19.0, 18.5.

IR (KBr, cm^{-1}): 3504, 2937, 2912, 1580, 1499, 957.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{20}ClN_4$: 339.1371, Found: 339.1381.



(E)-*6-(4-Chloro-2-(prop-1-en-1-yl)phenyl)-9-isobutyl-9H-purine* **(9af)**: was prepared according to the general procedure **3.1** (12 h). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **9ab** (24 mg) in 73% yield.

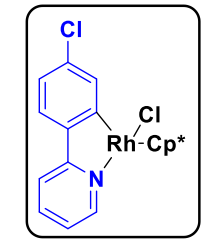
Physical State: colorless liquid
R_f-value: 0.3 (20% EtOAc/hexane)

^{1}H NMR ($CDCl_3$, 700 MHz): δ 9.06 (s, 1H), 8.06 (s, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.67 (s, 1H), 7.34 (d, J = 8.4 Hz, 1H), 6.62 (d, J = 15.4 Hz, 1H), 6.29-6.24 (m, 1H), 4.14 (d, J = 7.0 Hz, 2H), 2.38-2.32 (m, 1H), 1.79 (d, J = 6.3 Hz, 3H), 1.01 (d, J = 7.0 Hz, 6H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 157.5, 152.5, 152.4, 145.4, 139.3, 136.2, 132.9, 132.5, 131.7, 129.2, 128.4, 127.0, 126.6, 51.6, 29.4, 20.3, 19.0.

IR (KBr, cm^{-1}): 3455, 2927, 1708, 1586, 1327, 1107, 936.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}ClN_4$ 327.1371; Found 327.1372.



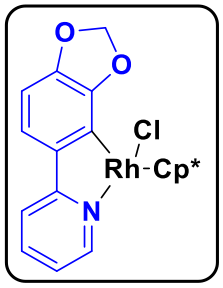
Intermediate-1 (Int-1): was prepared according to the general procedure **4.6**. The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **Int-1** (17 mg) in 73% yield.

Physical State: reddish solid
R_f-value: 0.5 (100% EtOAc)

^{1}H NMR ($CDCl_3$, 700 MHz): δ 8.71 (d, J = 5.6 Hz, 1H), 7.75 (d, J = 2.1 Hz, 1H), 7.72 (d, J = 3.5 Hz, 2H), 7.52 (d, J = 7.7 Hz, 1H), 7.17-7.14 (m, 1H), 7.04 (dd, J = 7.7 Hz, 1.4 Hz, 1H), 1.63 (s, 15H).

^{13}C{^{1}H} NMR ($CDCl_3$, 175 MHz): δ 180.3 (d, J = 32.9 Hz), 164.7, 151.6, 142.5, 137.6, 136.4, 136.0, 124.5, 123.4, 122.5, 119.5, 96.4 (d, J = 6.1 Hz), 9.4.

HRMS (ESI) m/z: $[M-Cl]^+$ Calcd for $C_{21}H_{22}ClNRh$ 426.0490; Found 426.0462.



Intermediate-2 (Int-2): was prepared according to the general procedure **4.7**. The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) giving **Int-2** (12 mg) in 50% yield.

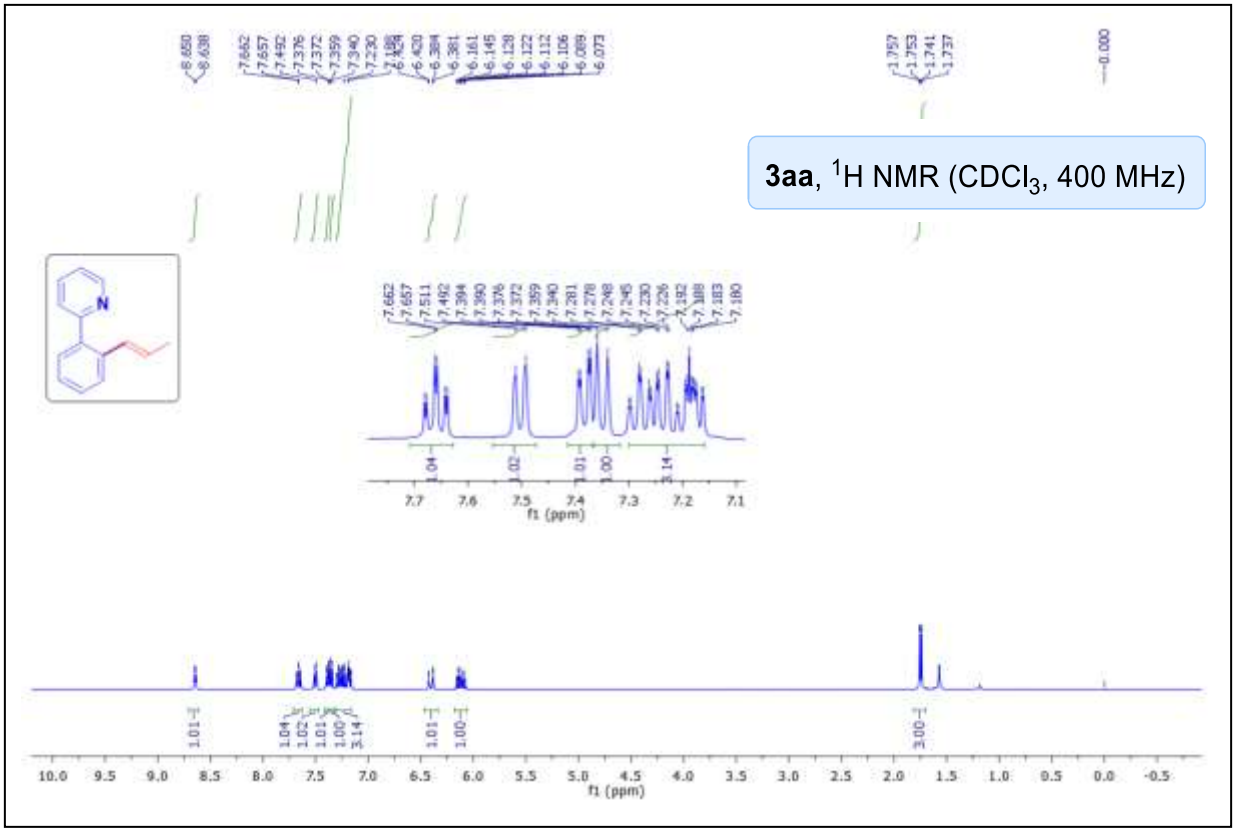
Physical State: reddish solid
R_f-value: 0.5 (100% EtOAc)

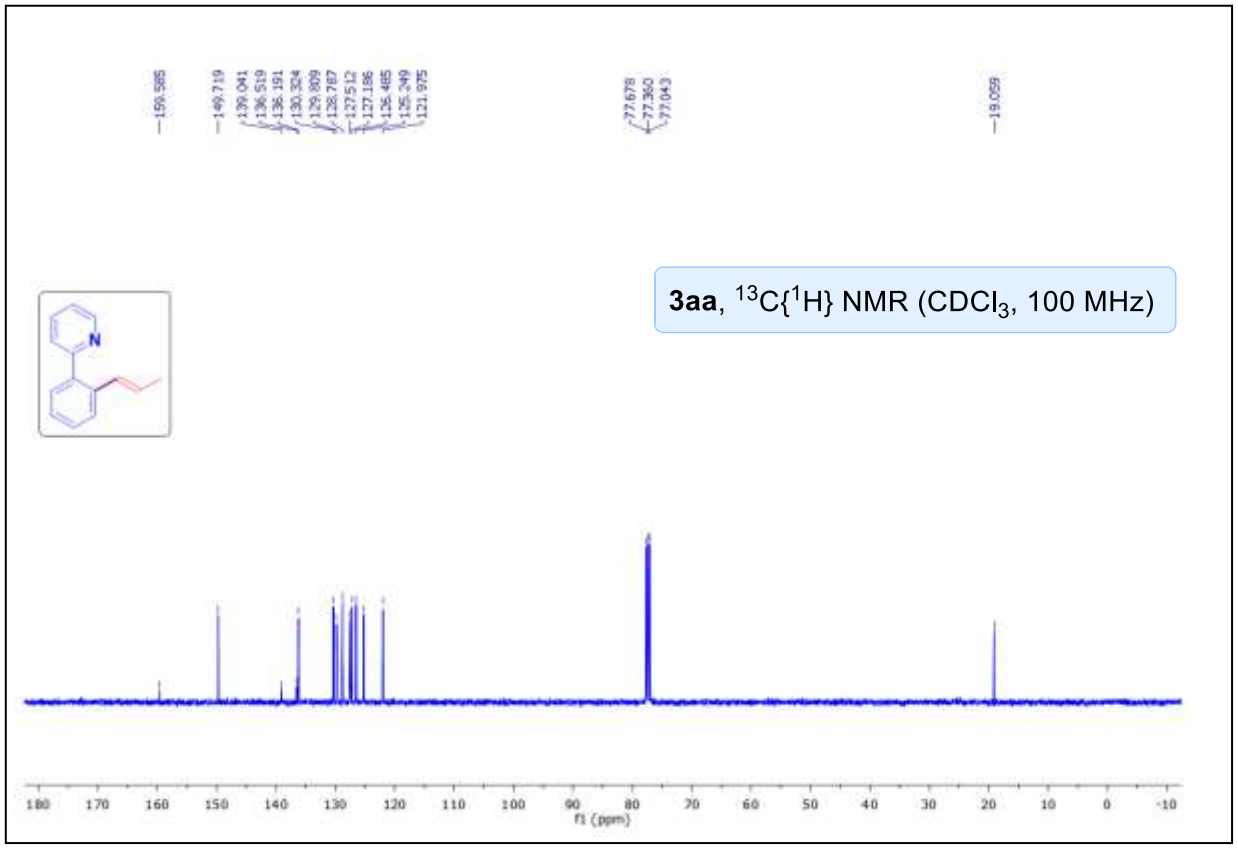
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66 (d, J = 5.6 Hz, 1H), 7.65 (dd, J = 4.8 Hz, 1.2 Hz, 2H), 7.28 (d, J = 8.0 Hz, 1H), 7.08-7.02 (m, 1H), 6.58 (d, J = 8.0 Hz, 1H), 6.04 (d, J = 1.6 Hz, 1H), 6.00 (d, J = 1.6 Hz, 1H), 1.67 (s, 15H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 165.7, 152.8, 152.6 (d, J = 23.2 Hz), 151.5, 147.6, 139.5, 137.2, 121.4, 119.4, 119.2, 104.3, 99.9, 96.8 (d, J = 6.3 Hz), 9.7.

HRMS (ESI) m/z: $[M\text{-}Cl]^+$ Calcd for $C_{22}H_{23}NO_2Rh$ 436.0778; Found 436.0772.

7. NMR spectra of the synthesized compounds (^{1}H, $^{13}C\{^{1}H\}$, and ^{19}F):





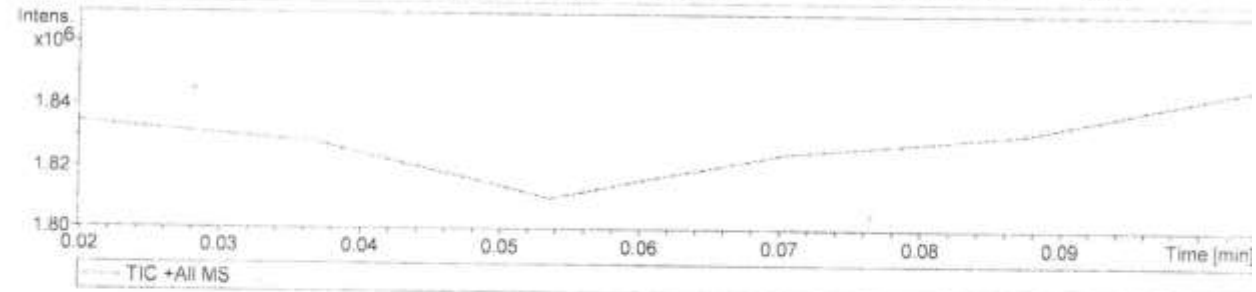
Display Report

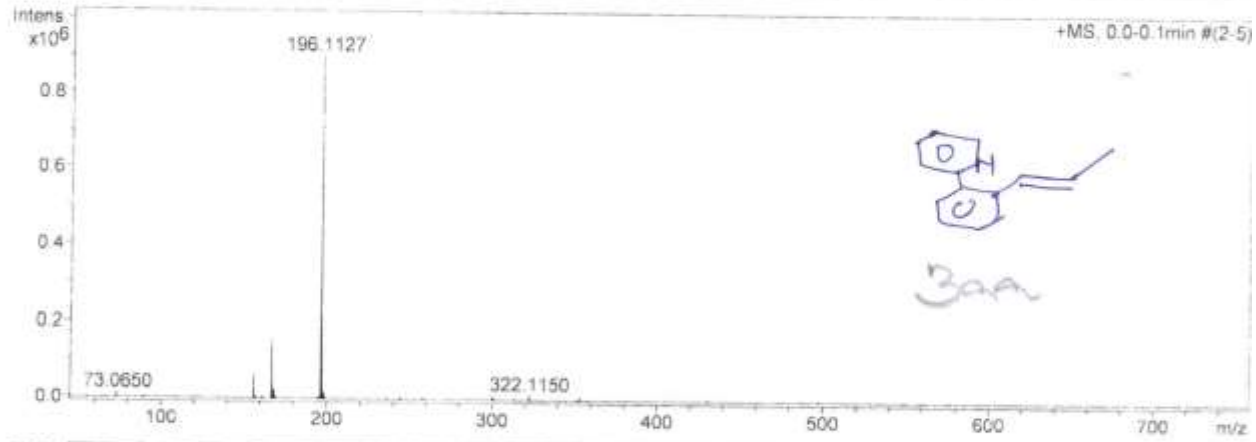
Analysis Info

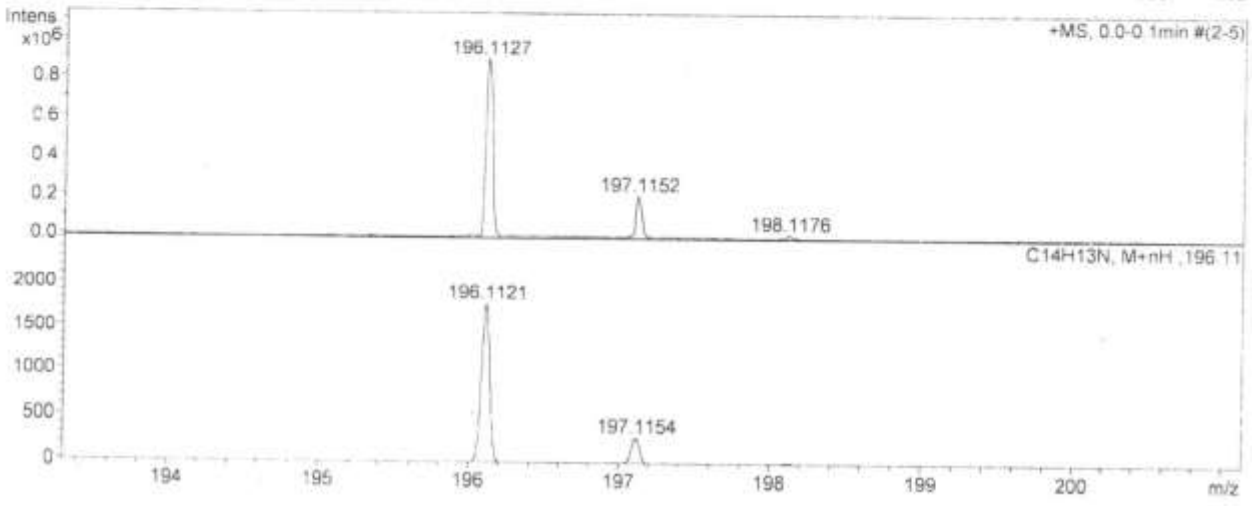
Analysis Name	D:\Data\NOV-2020\PCR\16112020_PCR_PB_1239_B.d	Acquisition Date	11/16/2020 3:30:49 PM
Method	Pos_tune_low m		
Sample Name	Tmix-131118	Operator	Amit S.Sahu
Comment		Instrument	micrOTOF-Q II 10337

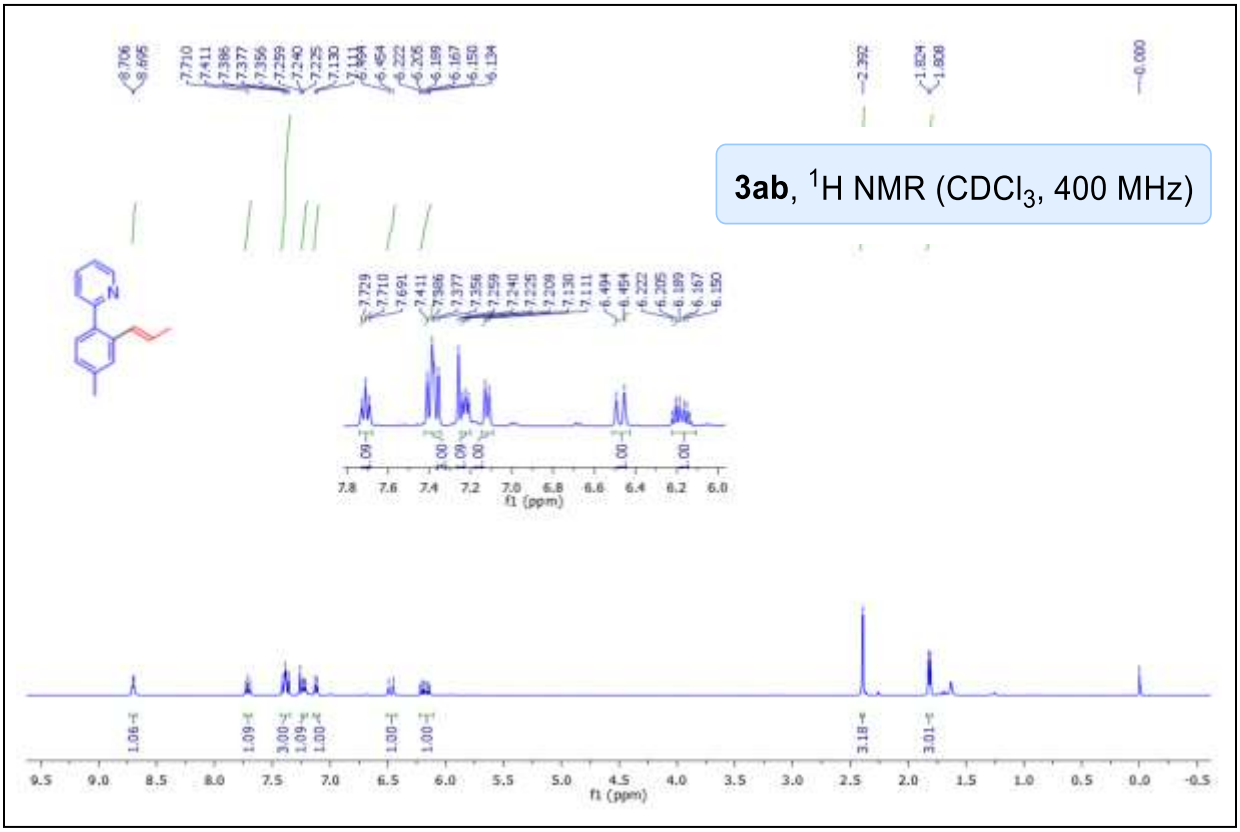
Acquisition Parameter

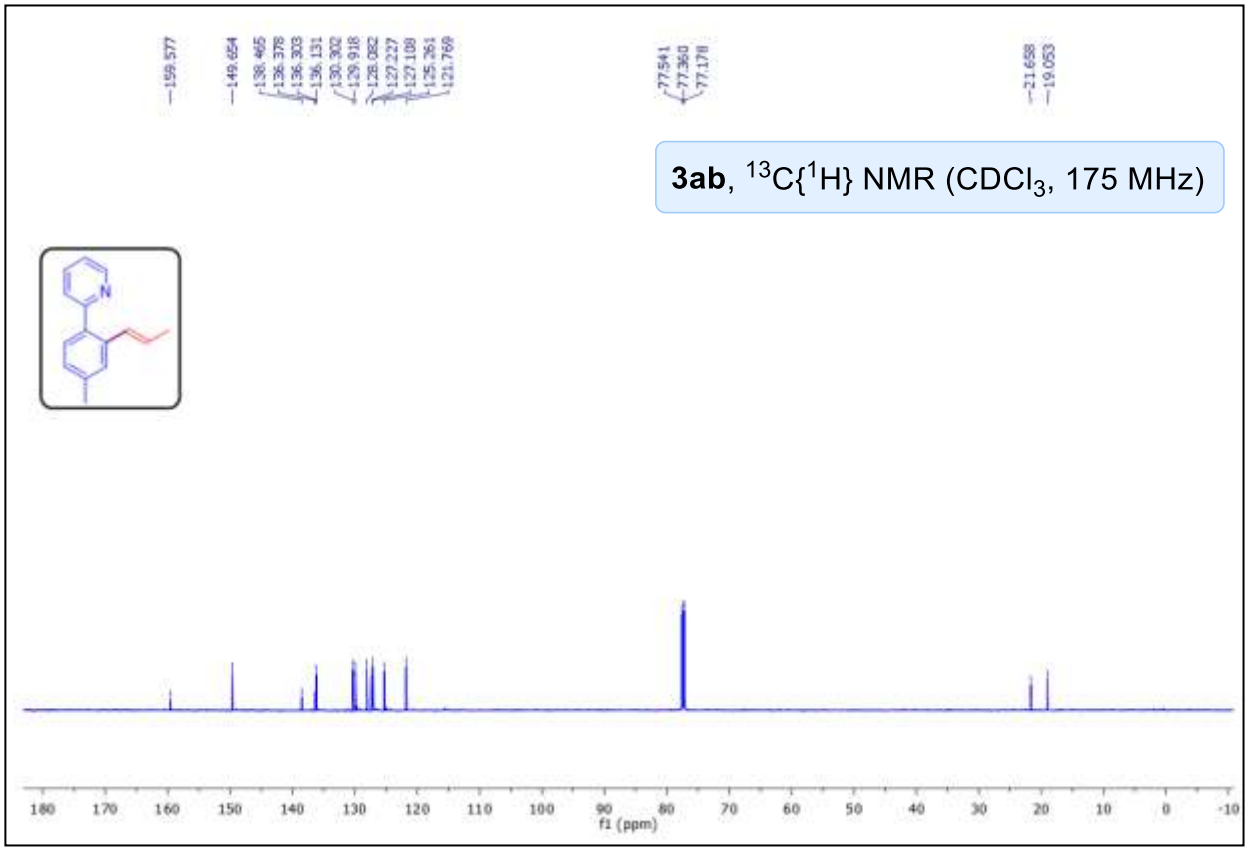
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








3ab, ^{1}H NMR ($CDCl_3$, 400 MHz)


3ab, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 175 MHz)

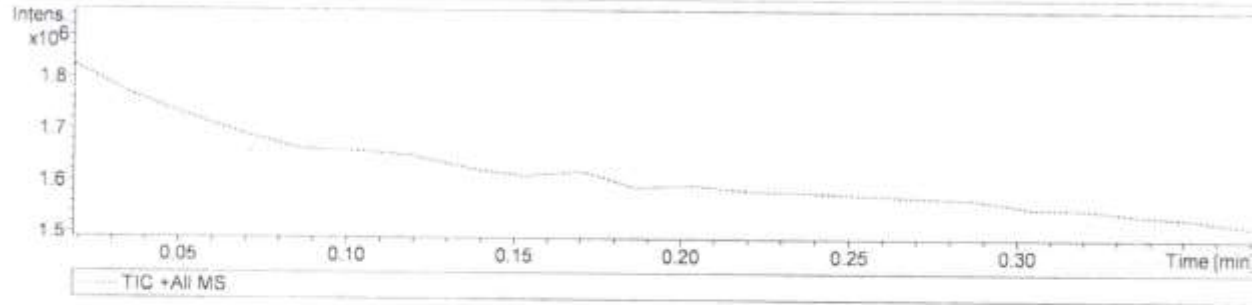
Display Report

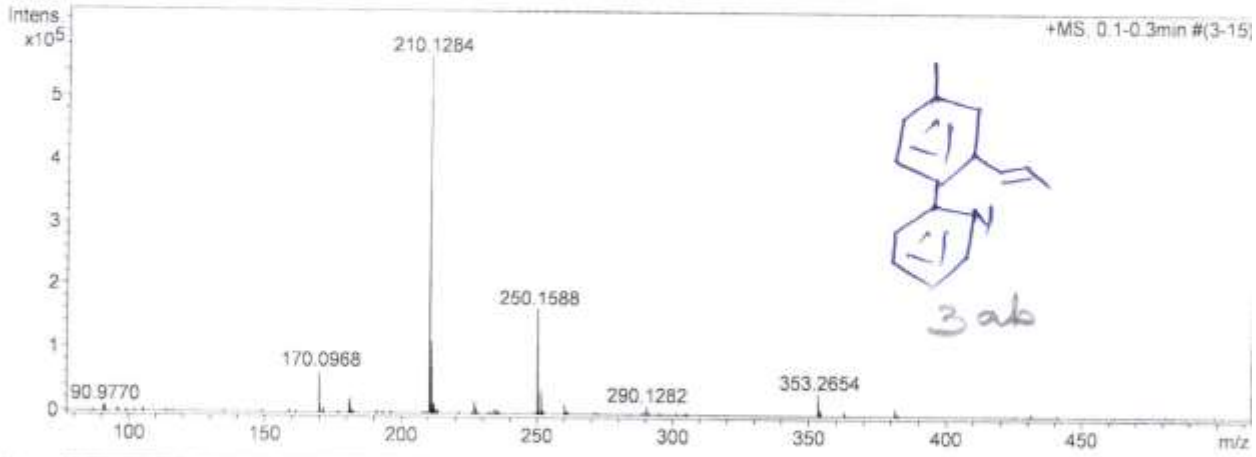
Analysis Info

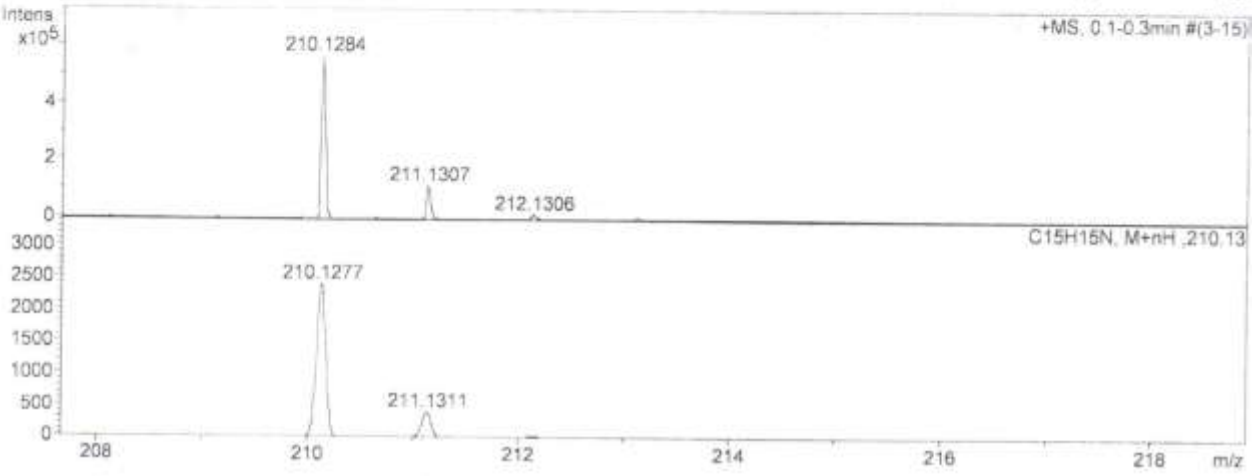
Analysis Name	D:\Data\MAR-2021\PCR\02032021_PCR_TN_1497.d	Acquisition Date	3/2/2021 10:54:05 AM
Method	Pos_tune_low.m	Operator	Amit S.Sahu
Sample Name	Tmix-131118	Instrument	micrOTOF-Q II 10337
Comment			

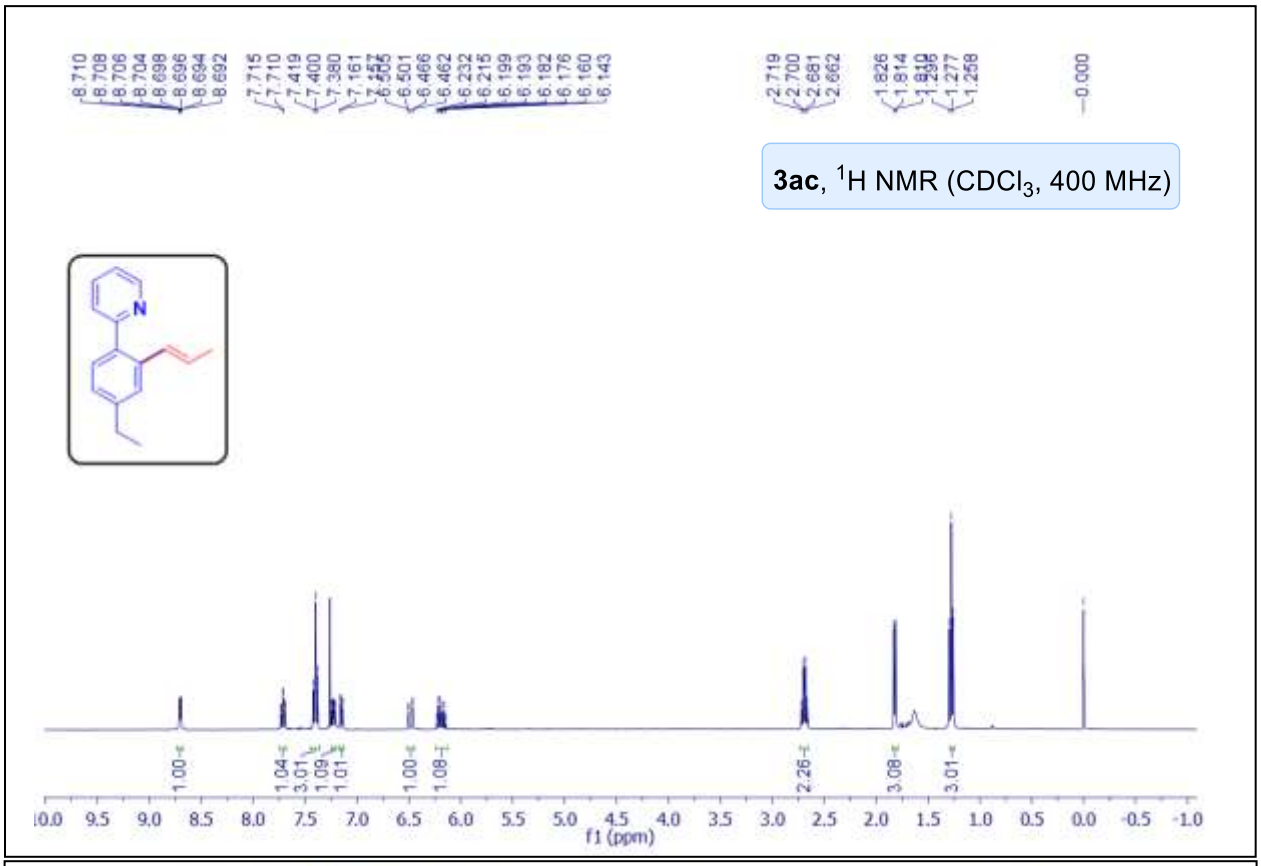
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

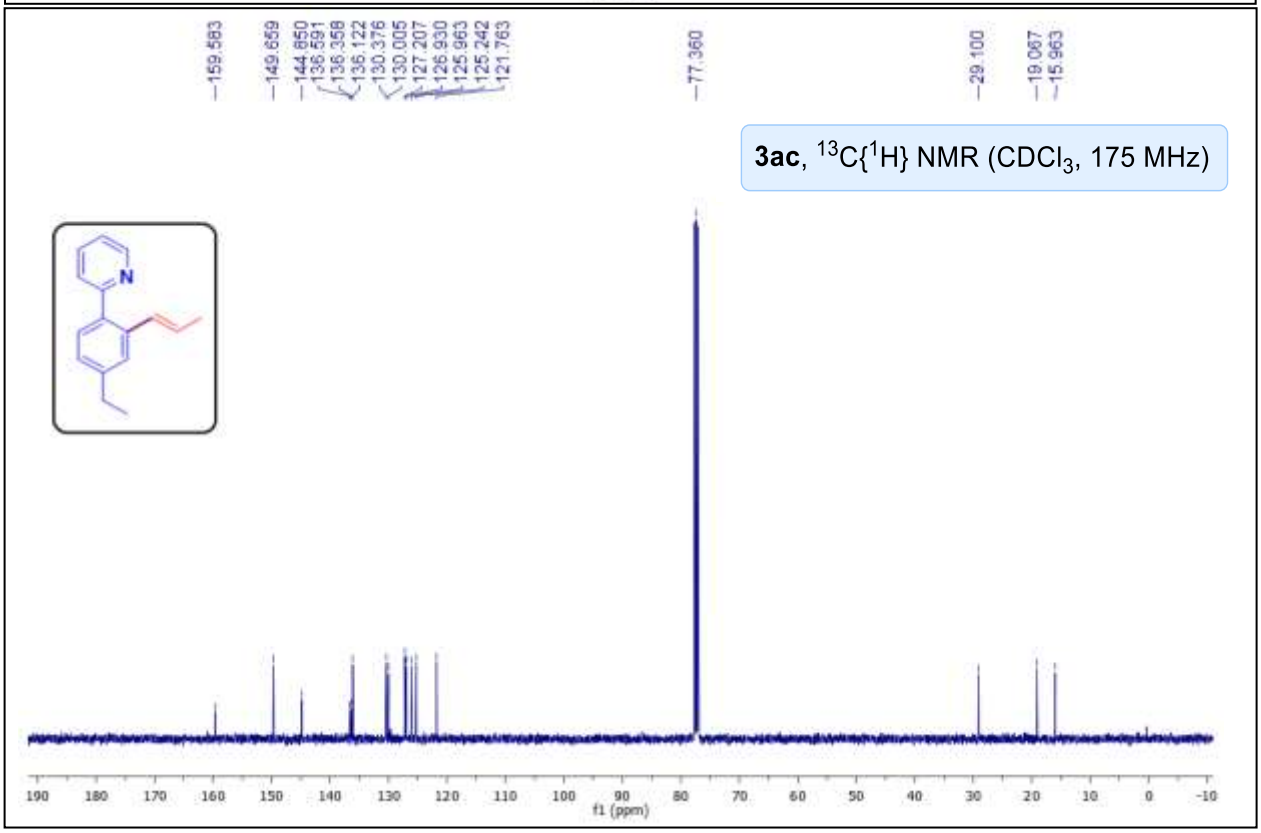








3ac, ^{1}H NMR ($CDCl_3$, 400 MHz)



3ac, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 175 MHz)

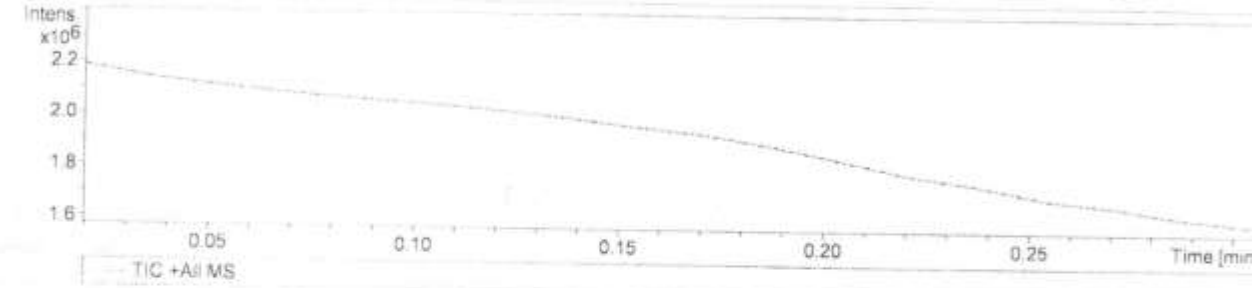
Display Report

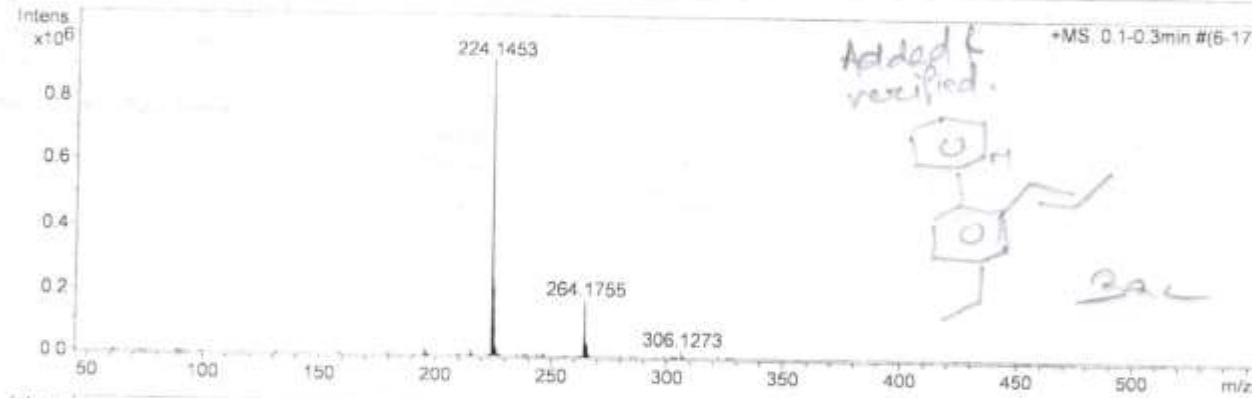
Analysis Info

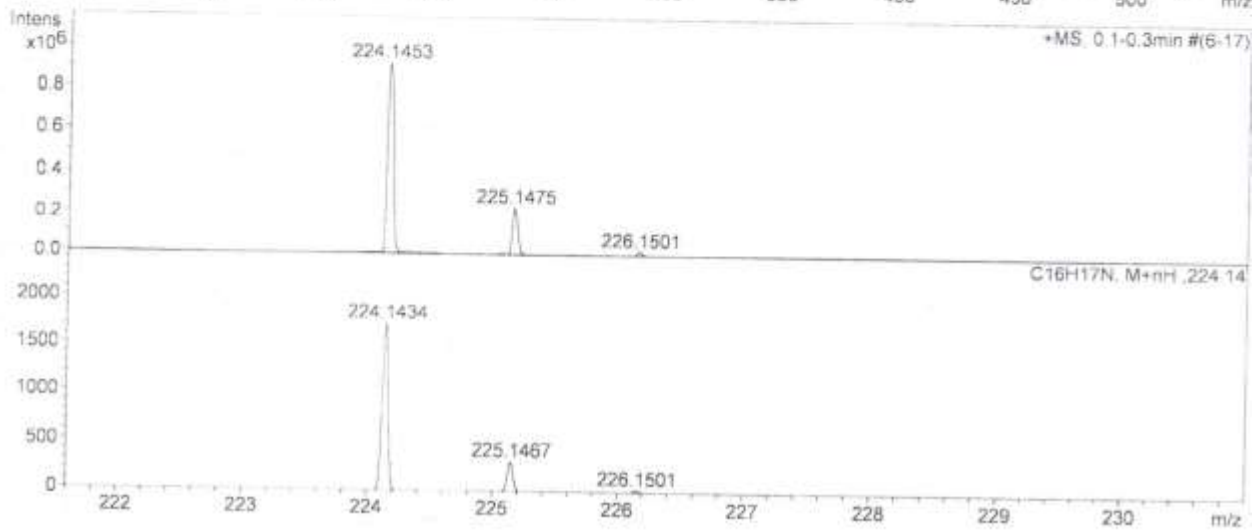
Analysis Name	D:\Data\MAR-2021\PCR\16032021_PCR_PB_1830.d	Acquisition Date	3/16/2021 3:28:48 PM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	Amit S.Sahu
Comment		Instrument	micrOTOF-Q II 10337

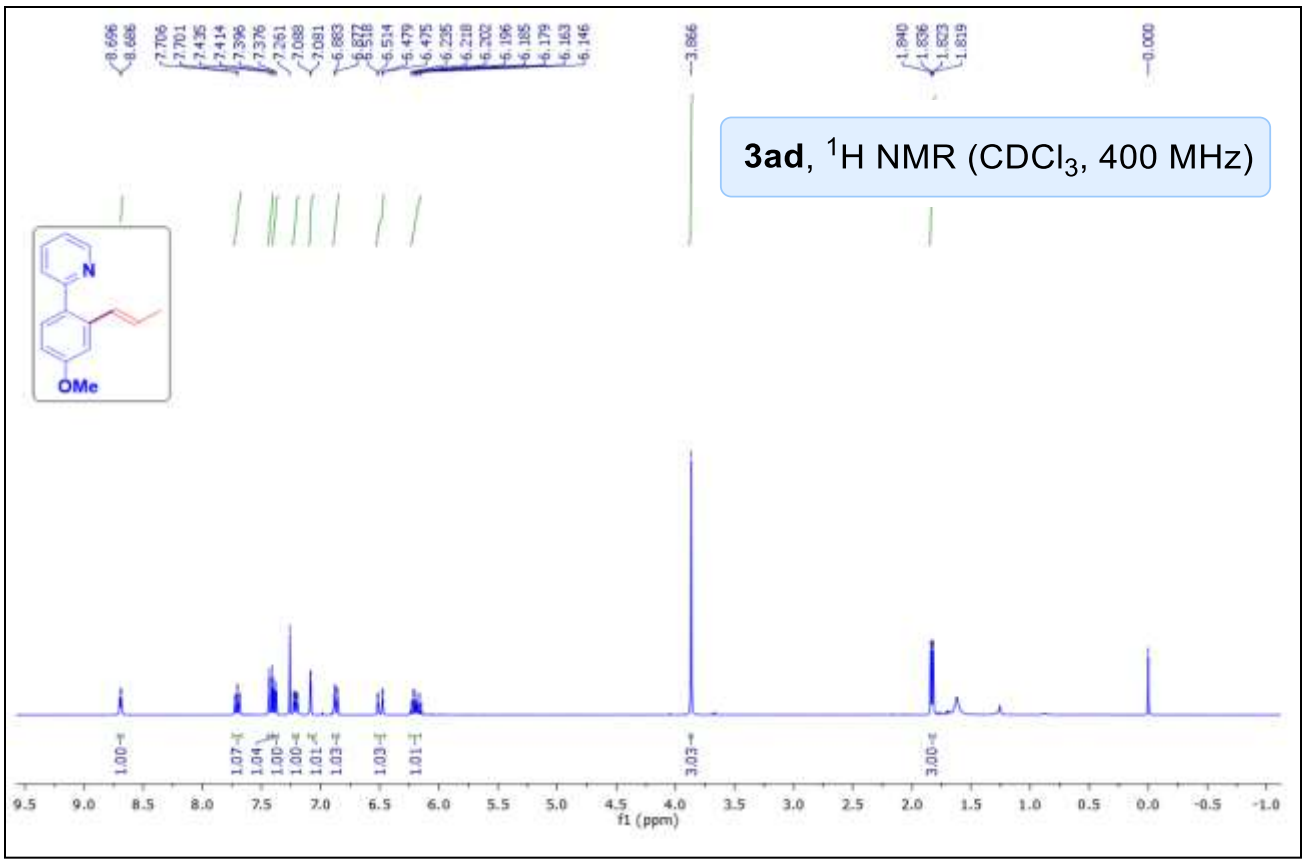
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

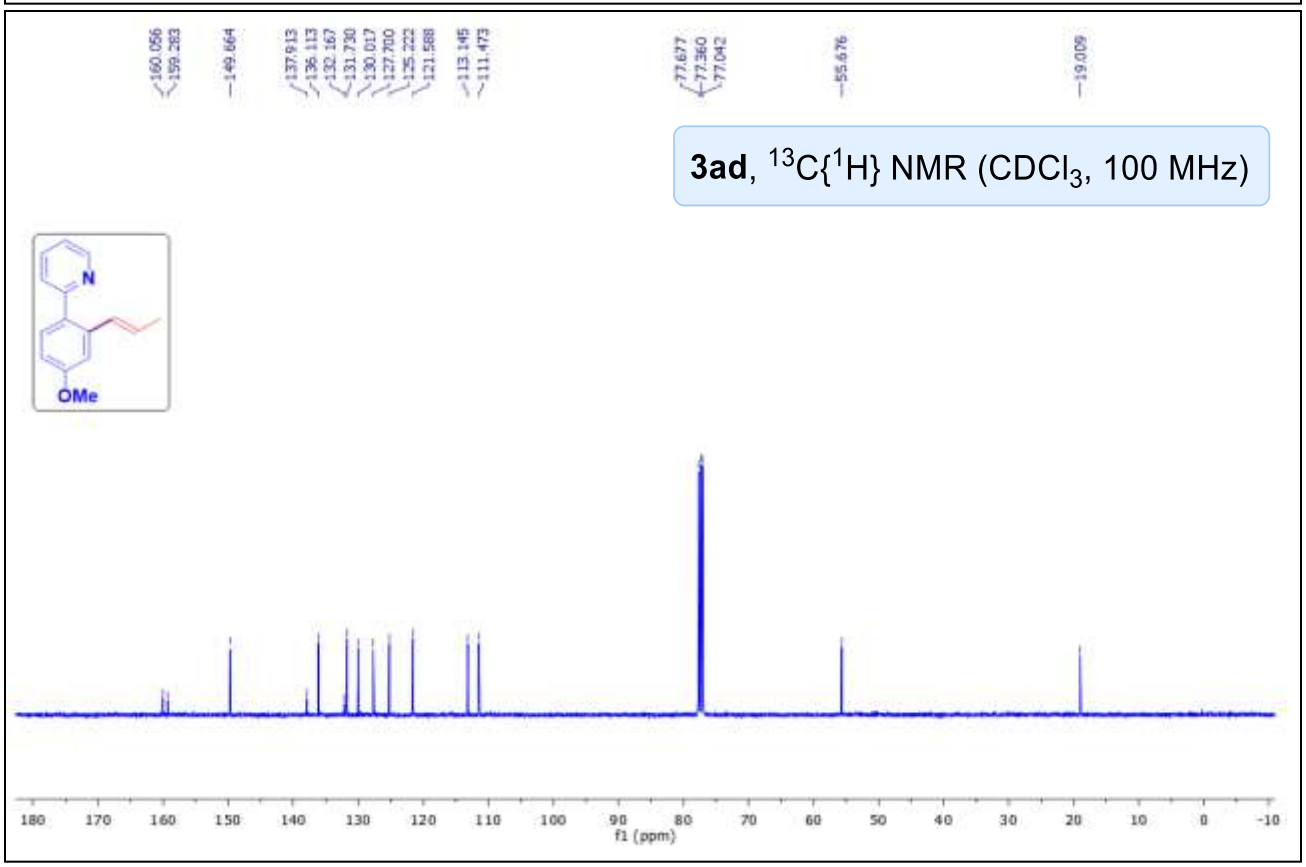








3ad, ^{1}H NMR ($CDCl_3$, 400 MHz)



3ad, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)

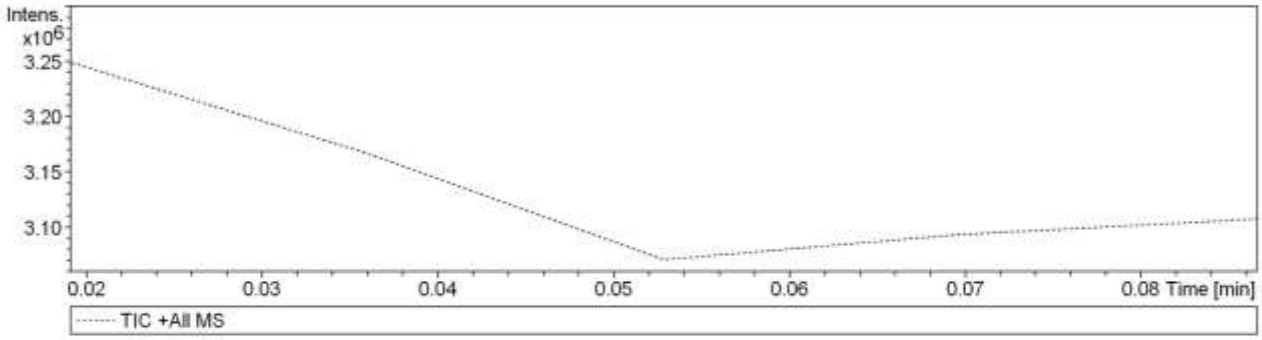
Display Report

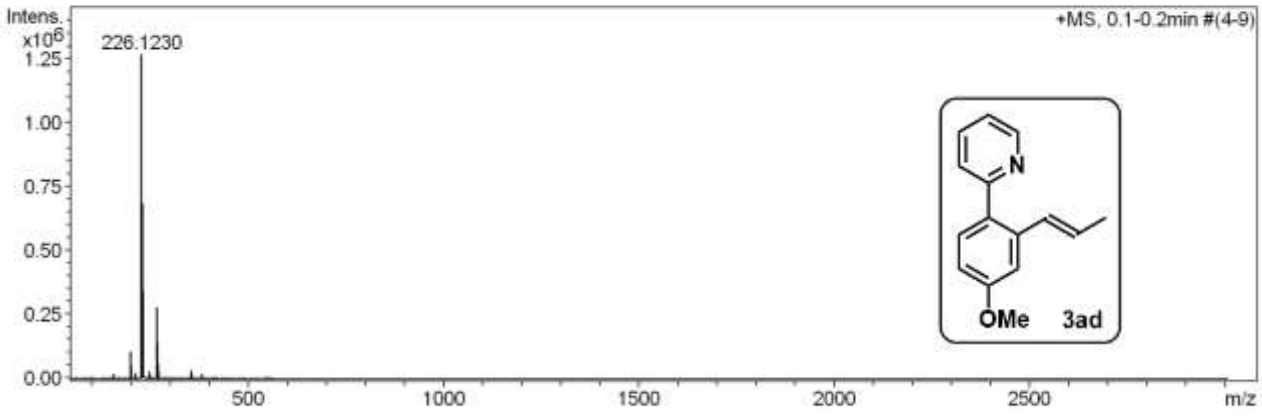
Analysis Info

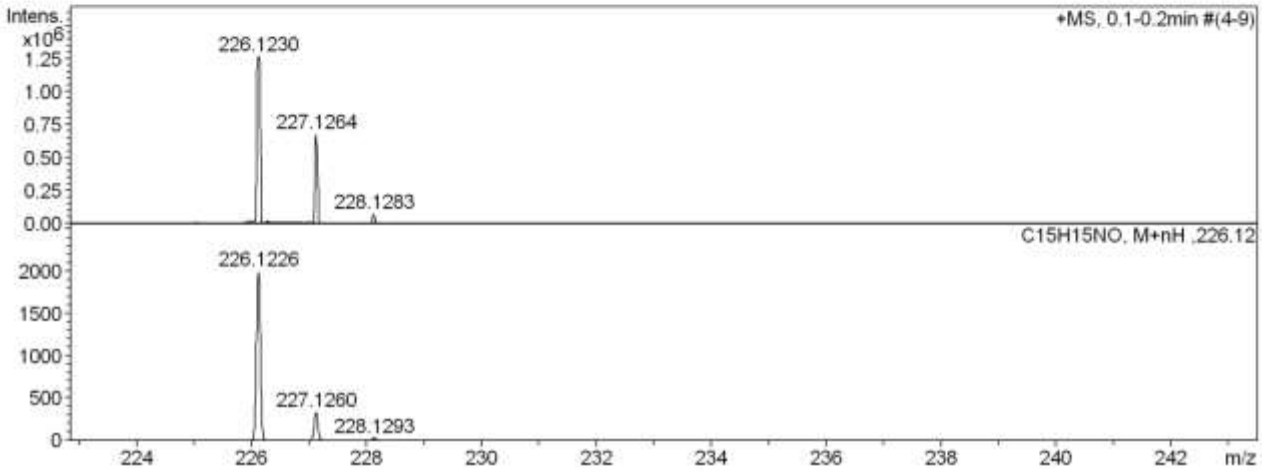
Analysis Name	D:\Data\FEB-2021\PCR\25022021_PCR_TN_1480.d	Acquisition Date	2/25/2021 11:28:17 AM
Method	Pos_tune_low.m	Operator	PRAKASH BEHERA
Sample Name	Tmix-131118	Instrument	micrOTOF-Q II 10337
Comment			

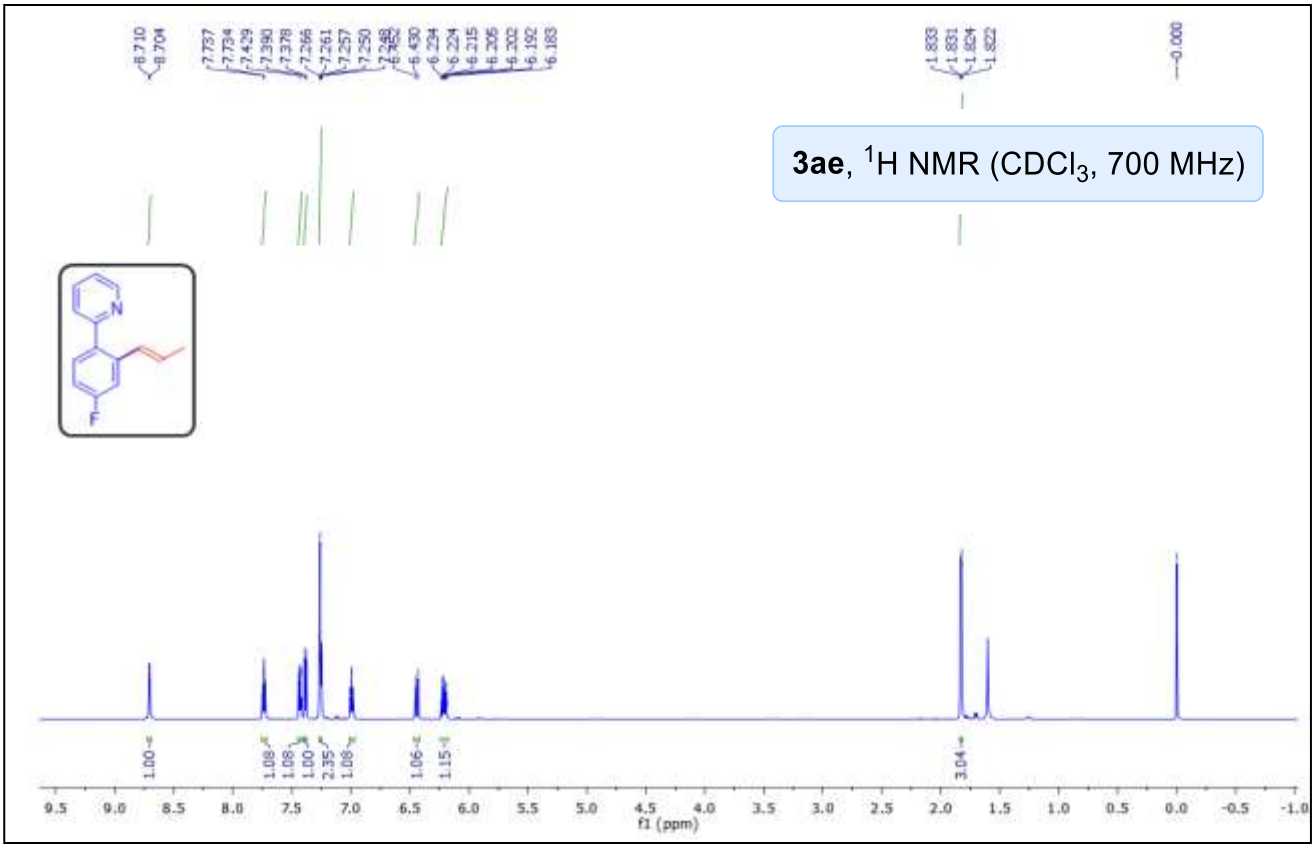
Acquisition Parameter

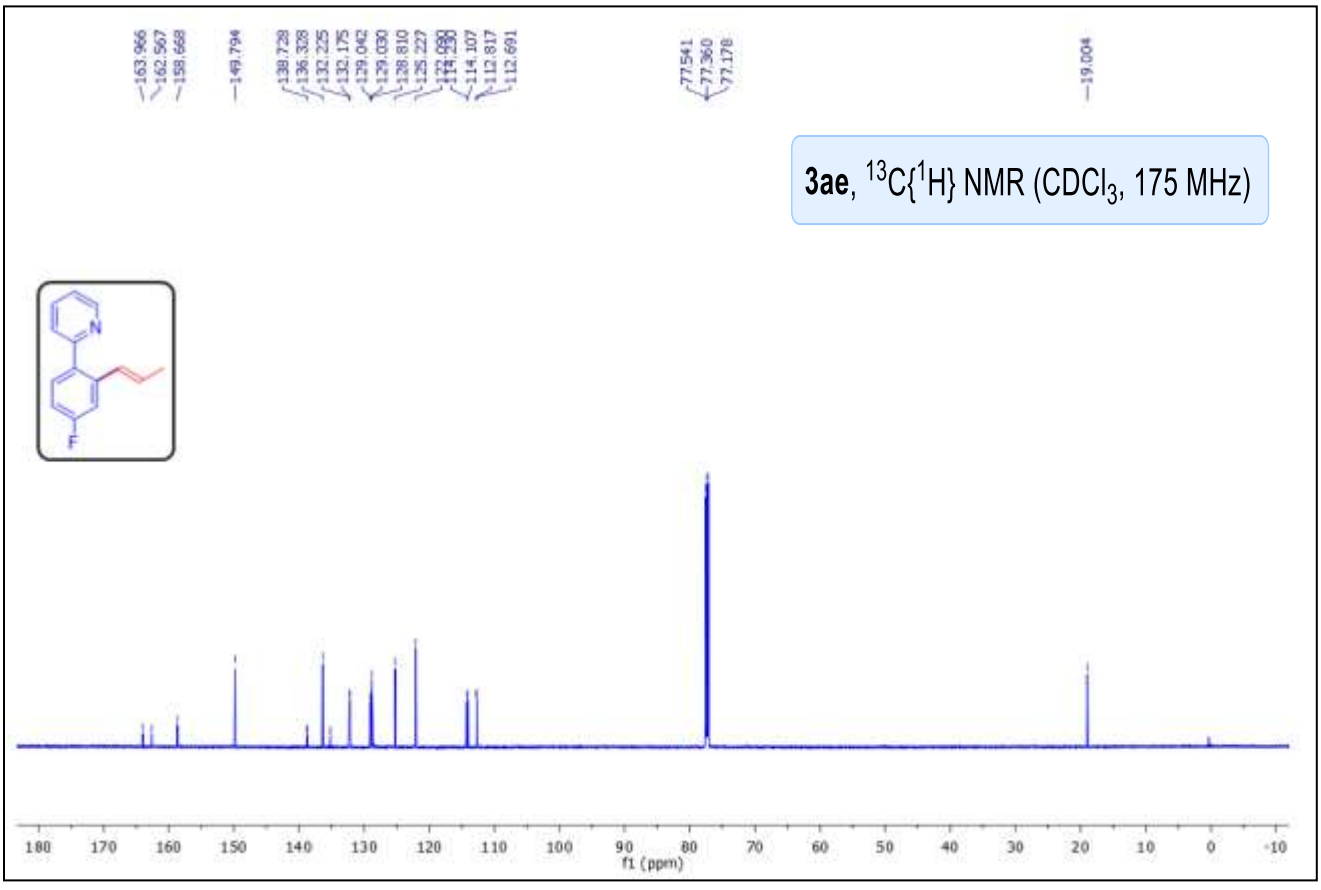
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

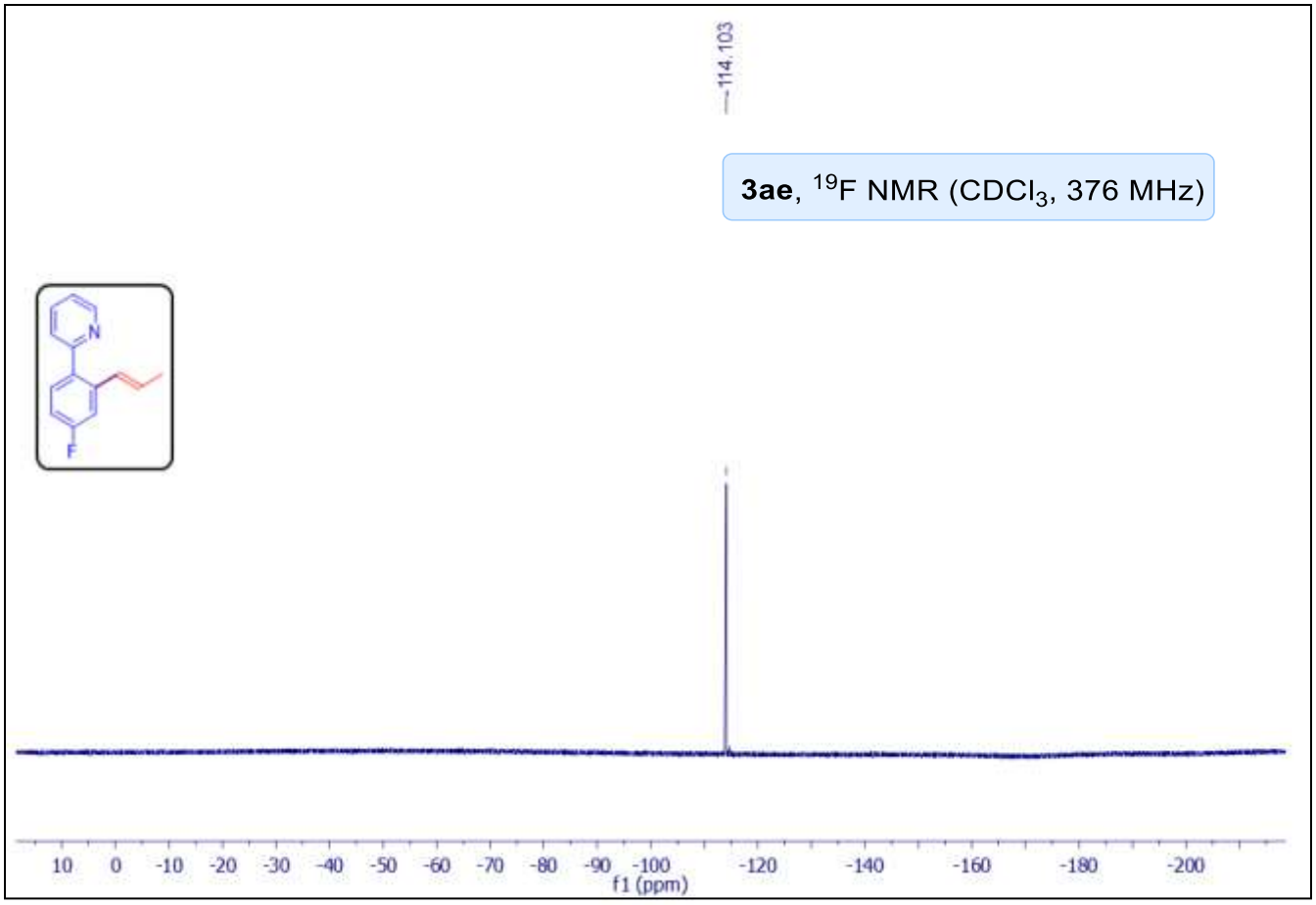







3ae, 1H NMR (CDCl3, 700 MHz)
f1 (ppm)


3ae, 13C{1H} NMR (CDCl3, 175 MHz)
f1 (ppm)


-114.103
3ae, 19F NMR (CDCl3, 376 MHz)
N
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

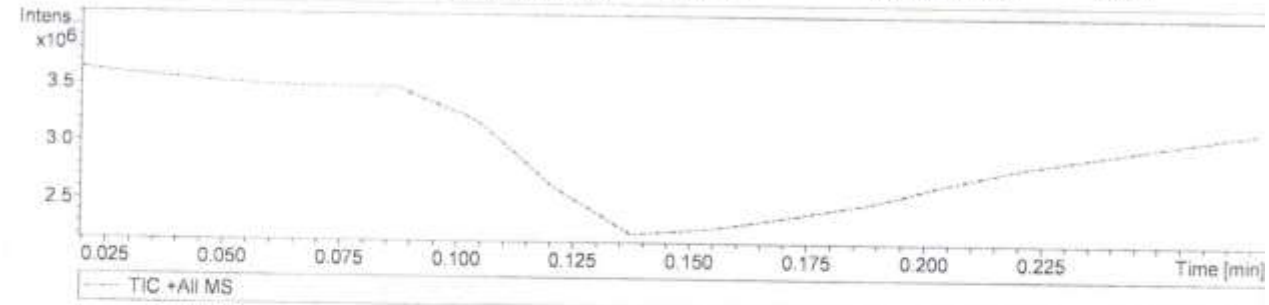
Display Report

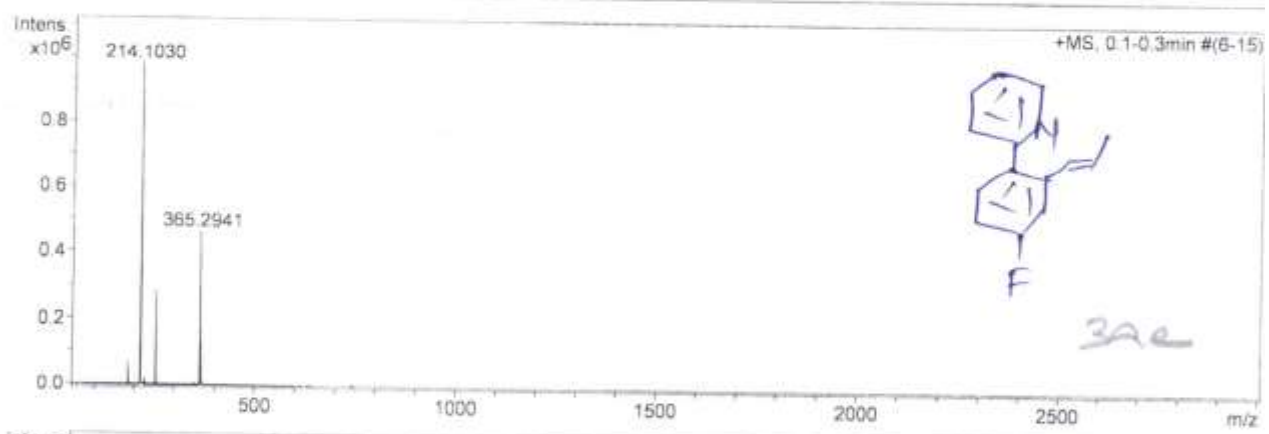
Analysis Info

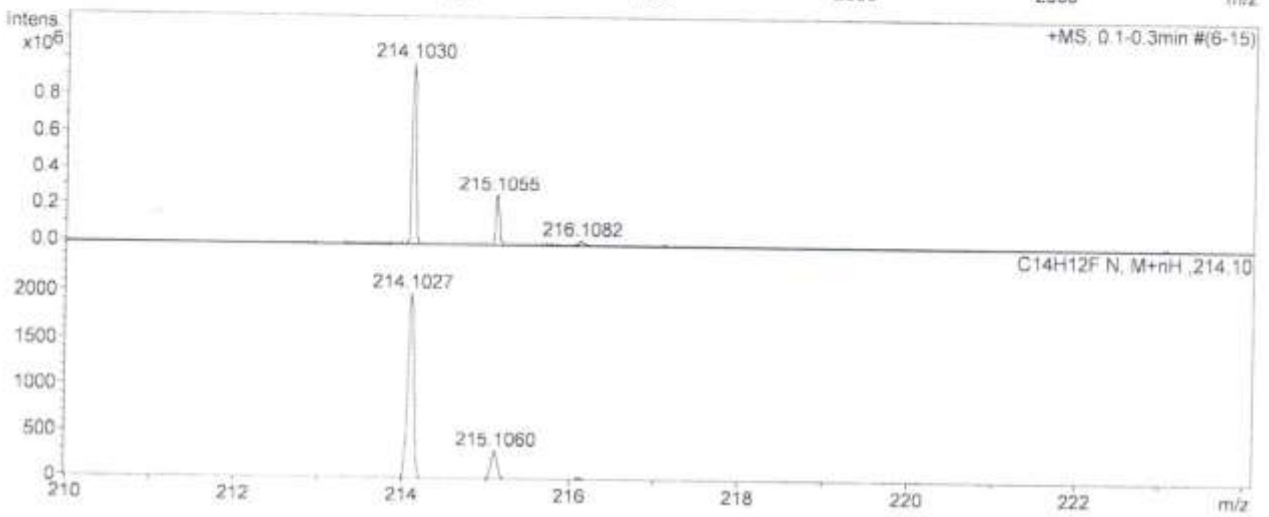
Analysis Name	D:\Data\FEB-2021\PCR\25022021_PCR_TN_1481.d	Acquisition Date	2/25/2021 12:40:26 PM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	PRAKASH BEHERA
Comment		Instrument	micrOTOF-Q II 10337

Acquisition Parameter

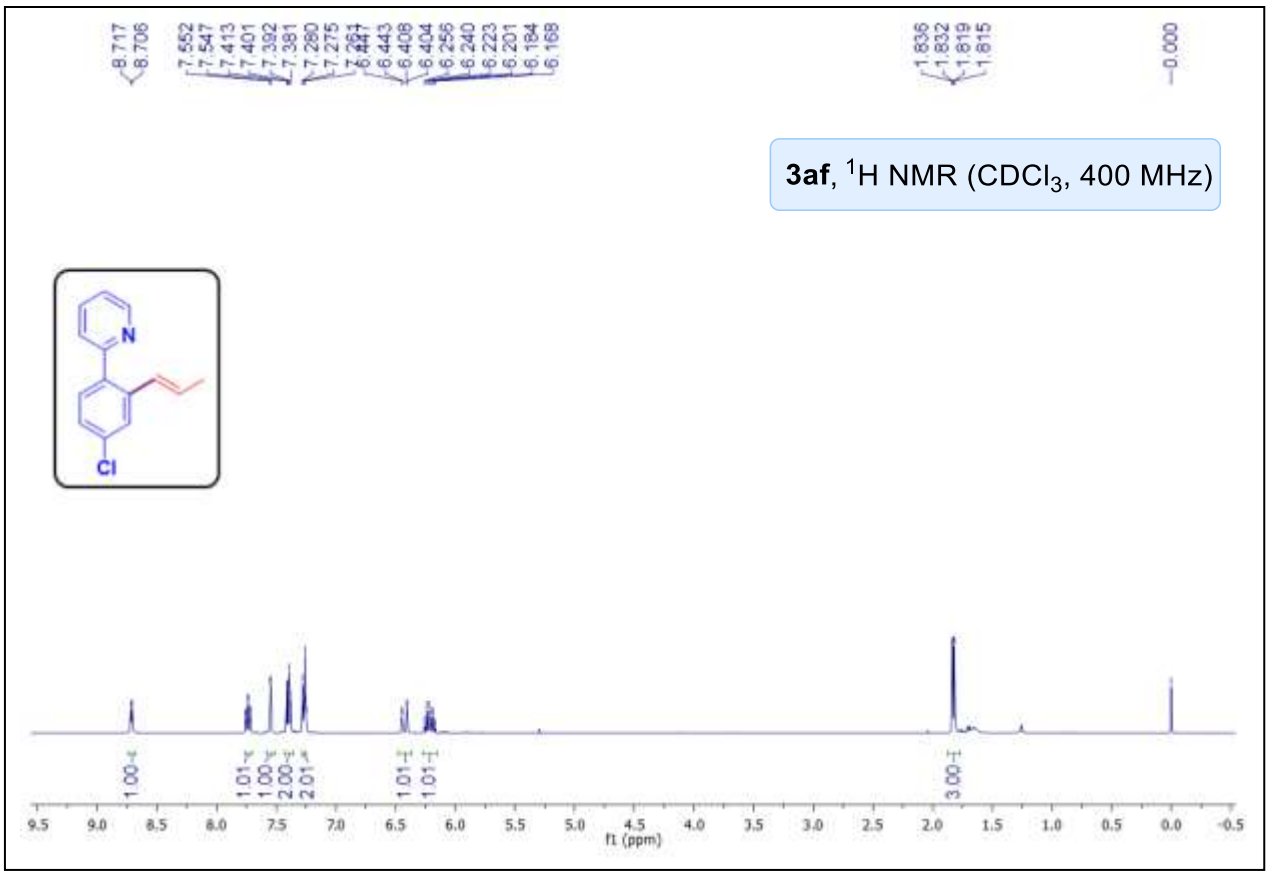
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



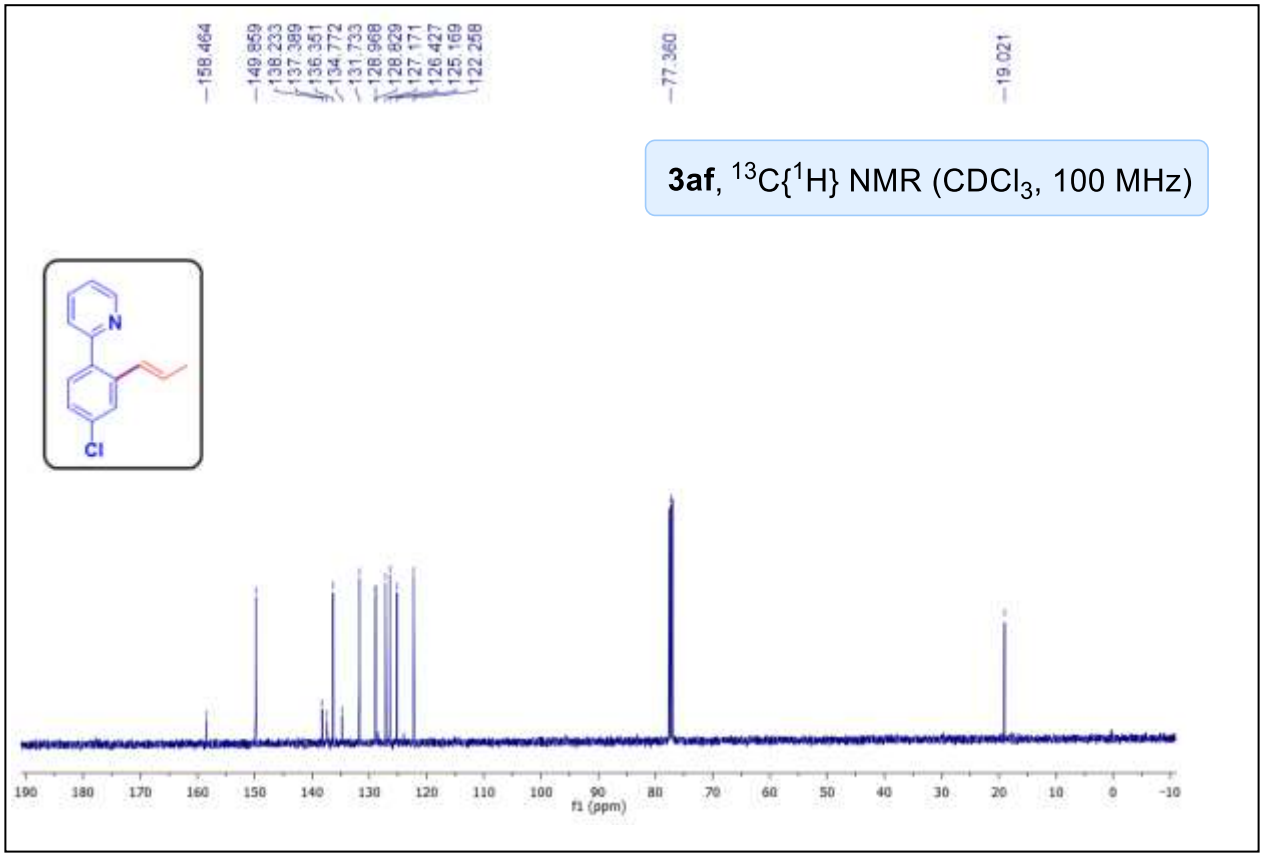




Bruker Compass DataAnalysis 4.0 printed 2/25/2021 12:41:59 PM Page 1 of 1



3af, ^{1}H NMR ($CDCl_3$, 400 MHz)



3af, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)

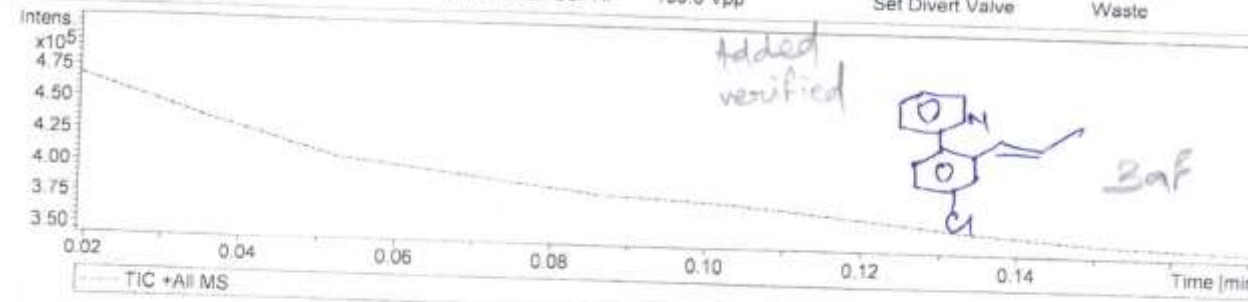
Display Report

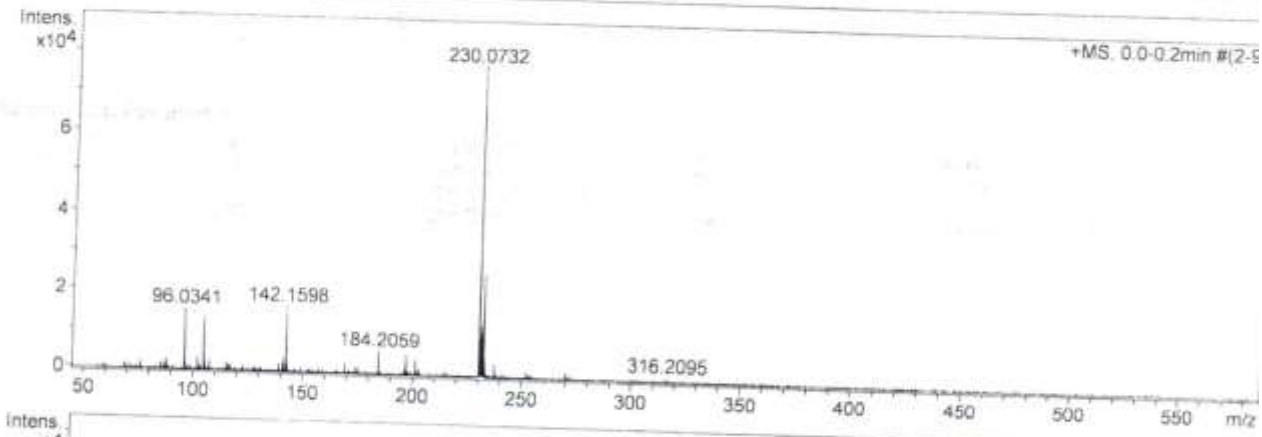
Analysis Info

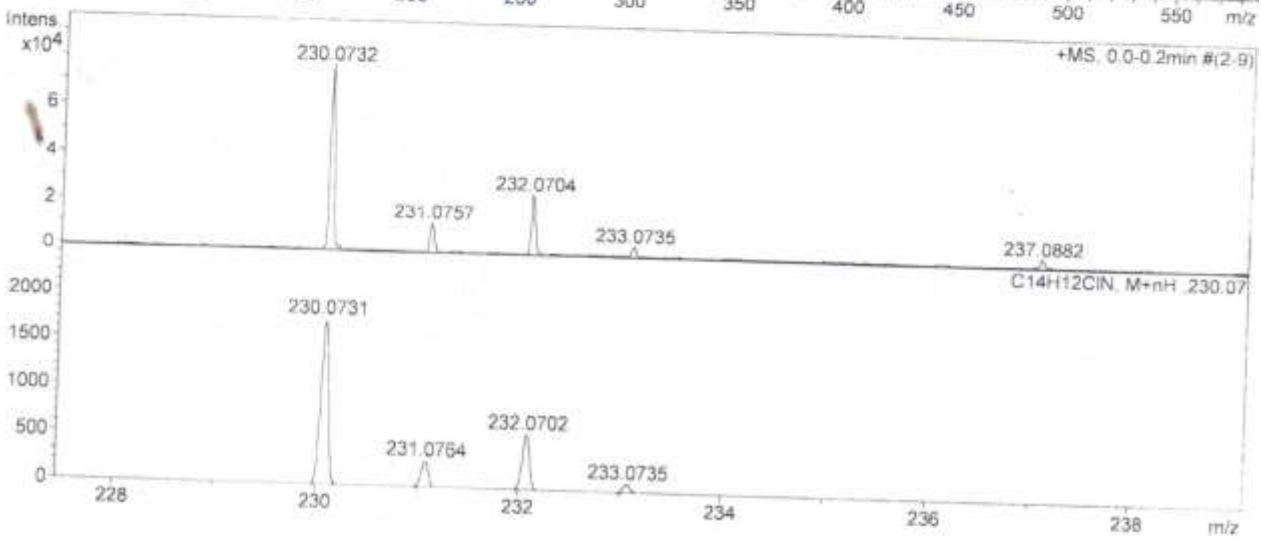
Analysis Name	D:\Data\JAN-2021\AS\05012021_PCR_PB_1627.d	Acquisition Date	1/5/2021 11:59:03 AM
Method	Pos_tune_low_05122019.m		
Sample Name	Tmix-131118	Operator	Amit S.Sahu
Comment		Instrument	micrOTOF-Q II 10337

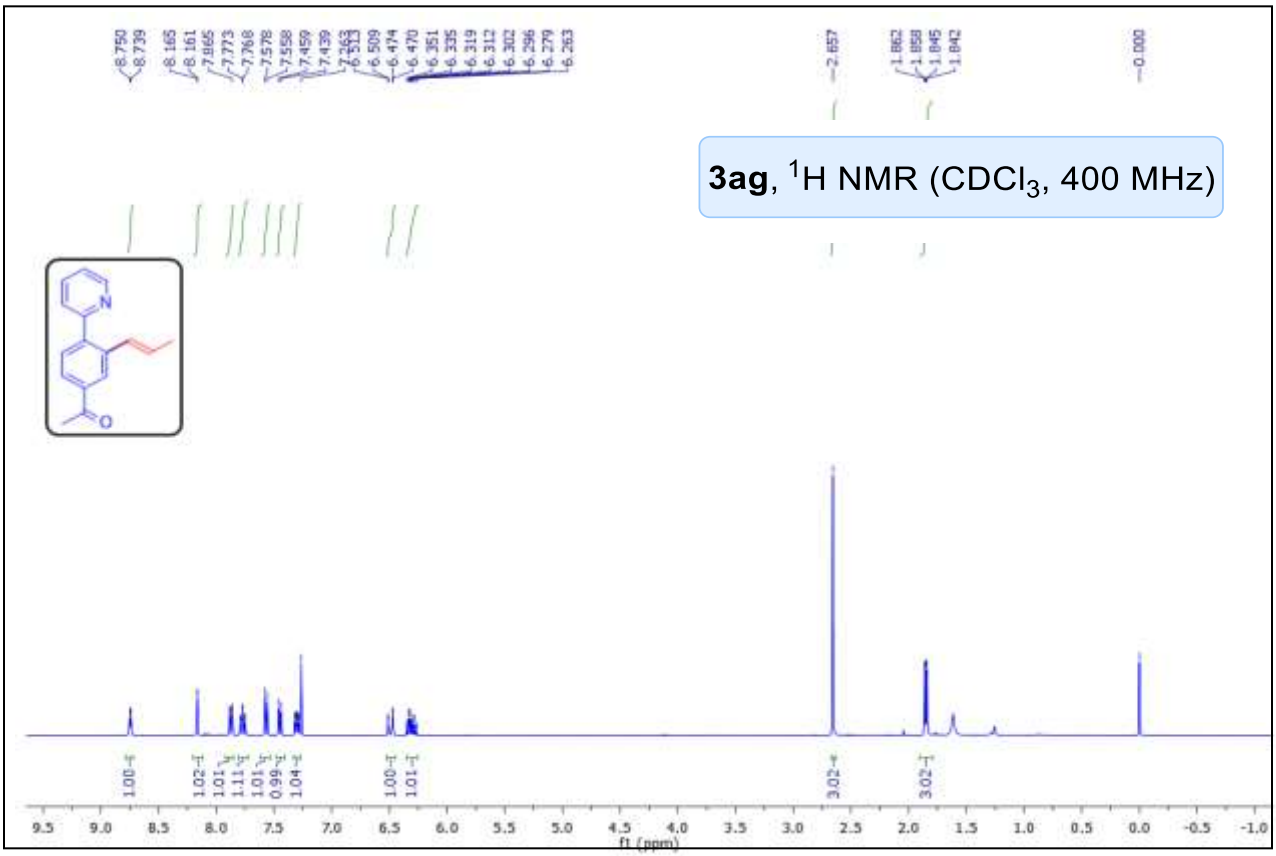
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.5 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

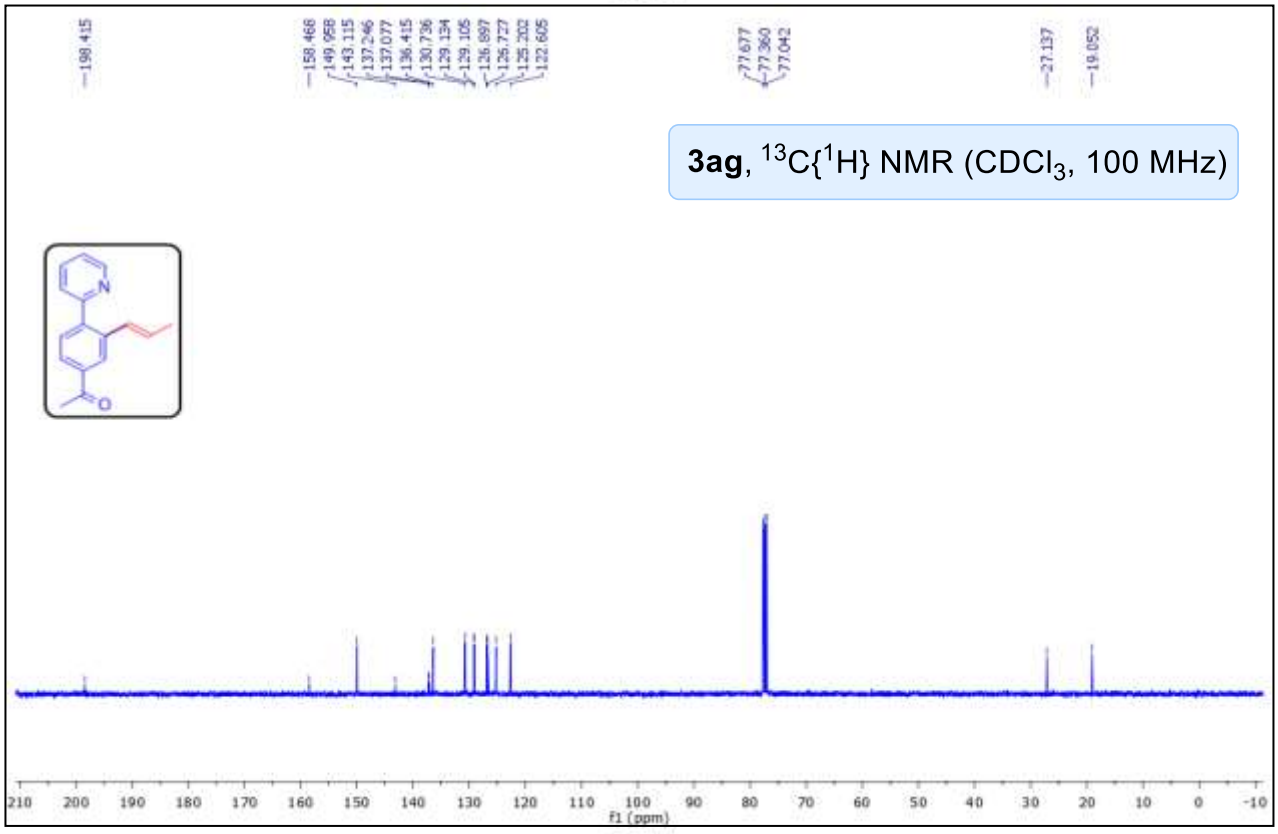








3ag, ^{1}H NMR ($CDCl_3$, 400 MHz)



3ag, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)

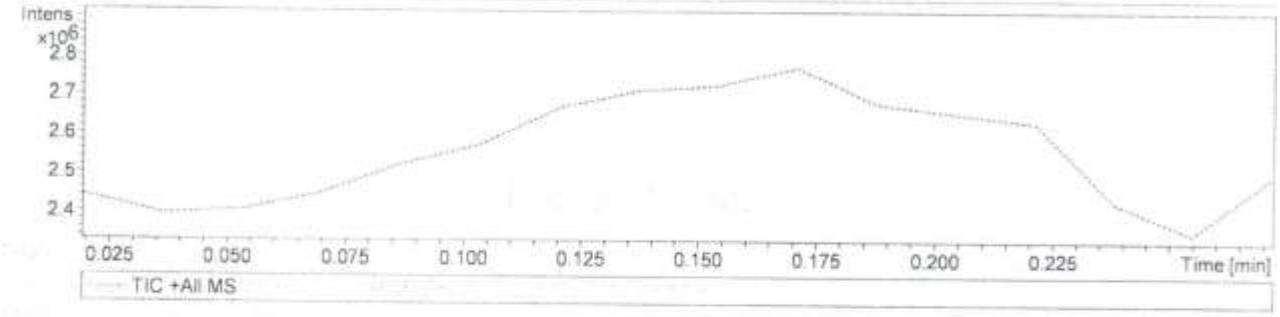
Display Report

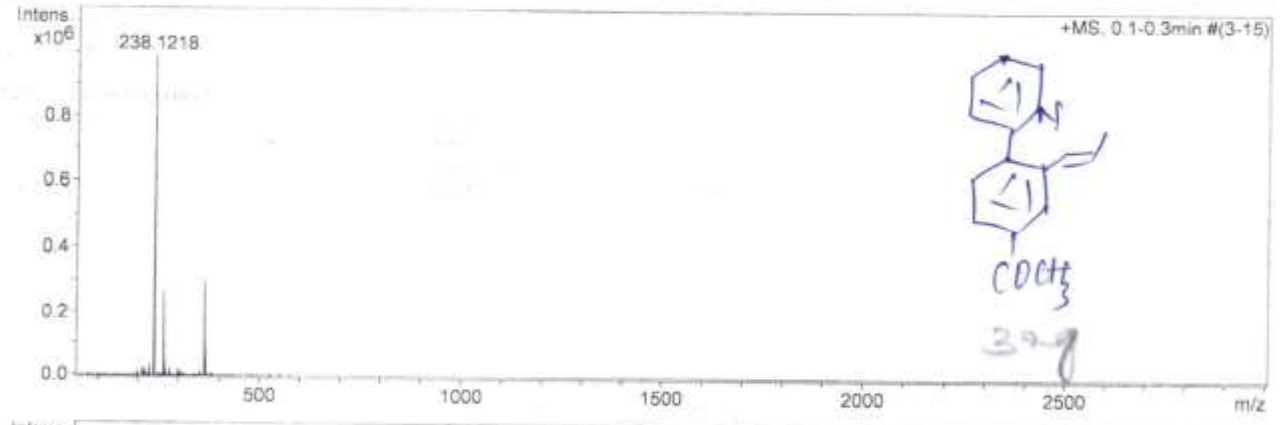
Analysis Info

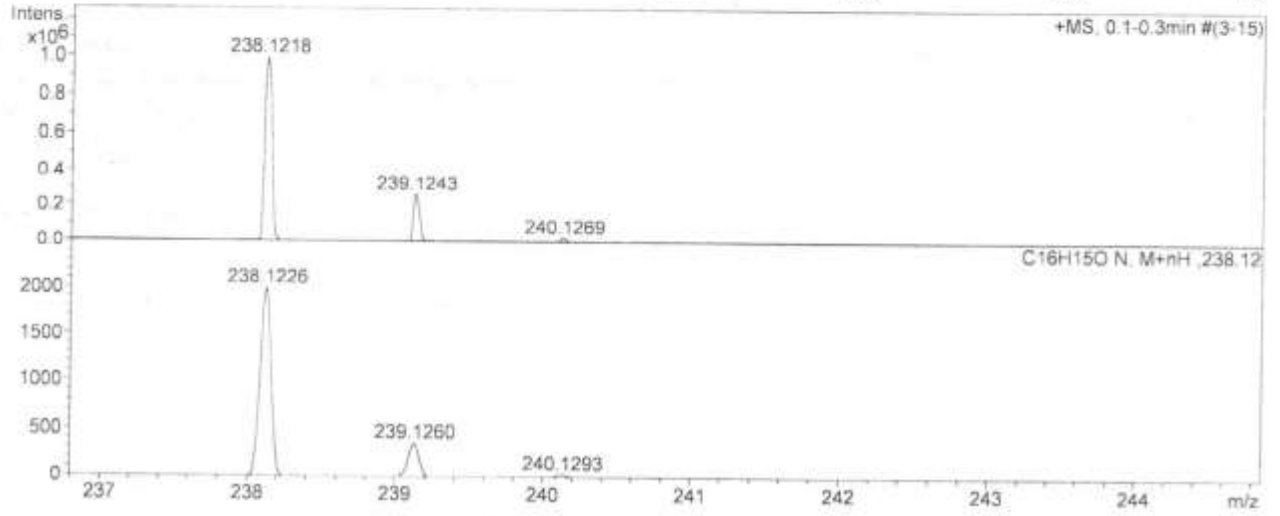
Analysis Name	D:\Data\FEB-2021\PCR\25022021_PCR_TN_1483.d	Acquisition Date	2/25/2021 2:48:31 PM
Method	Pos_tune_low.m	Operator	PRAKASH BEHERA
Sample Name	Tmix-131118	Instrument	micrOTOF-Q II 10337
Comment			

Acquisition Parameter

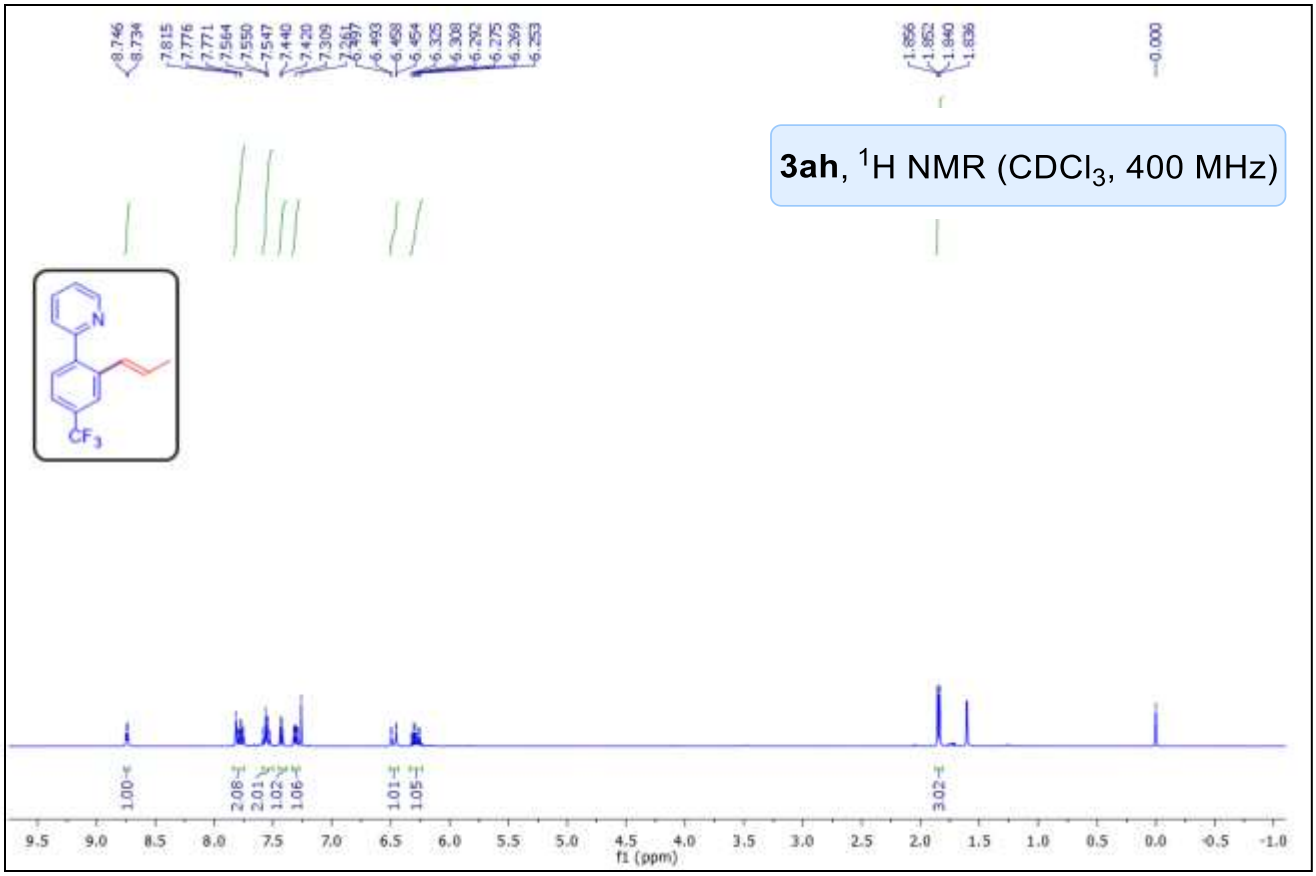
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

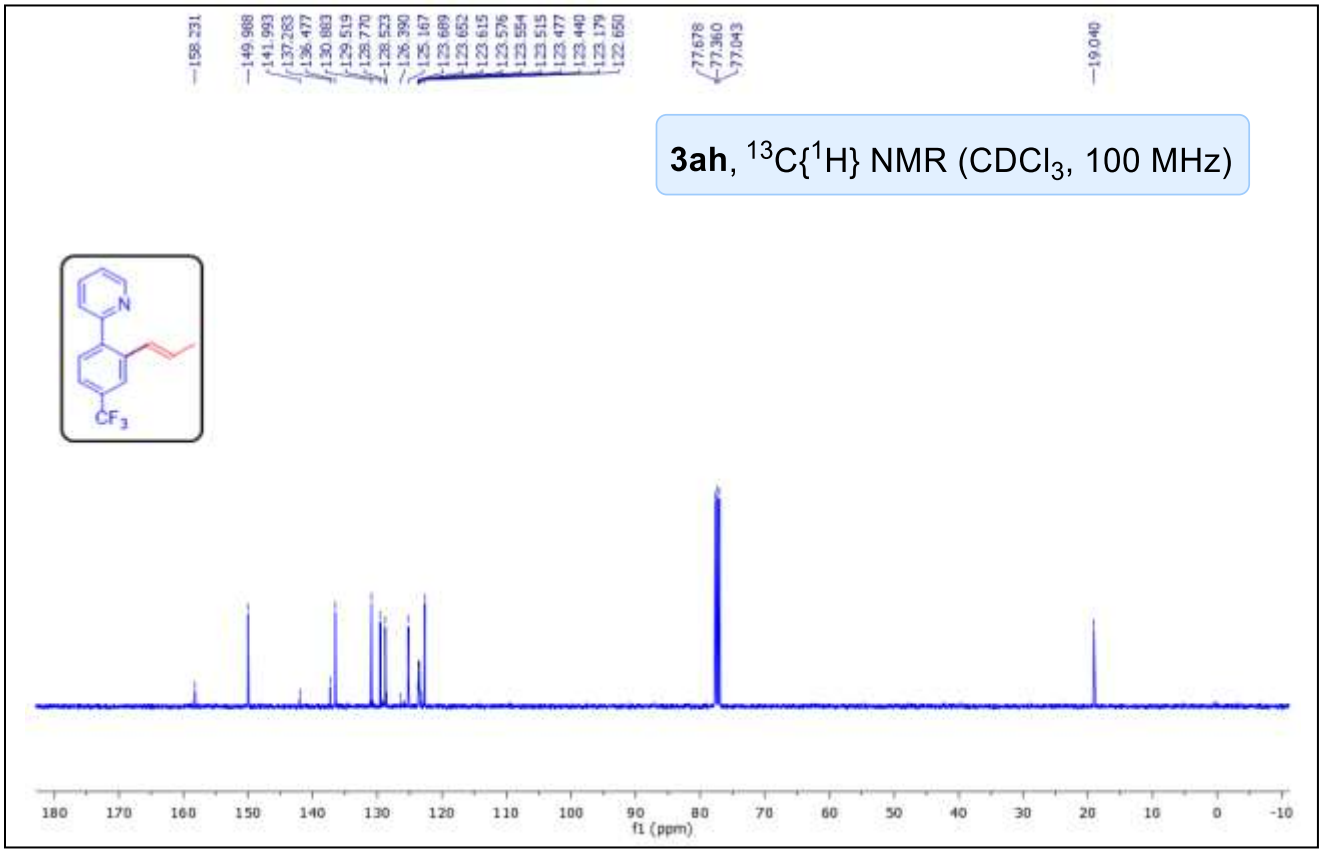


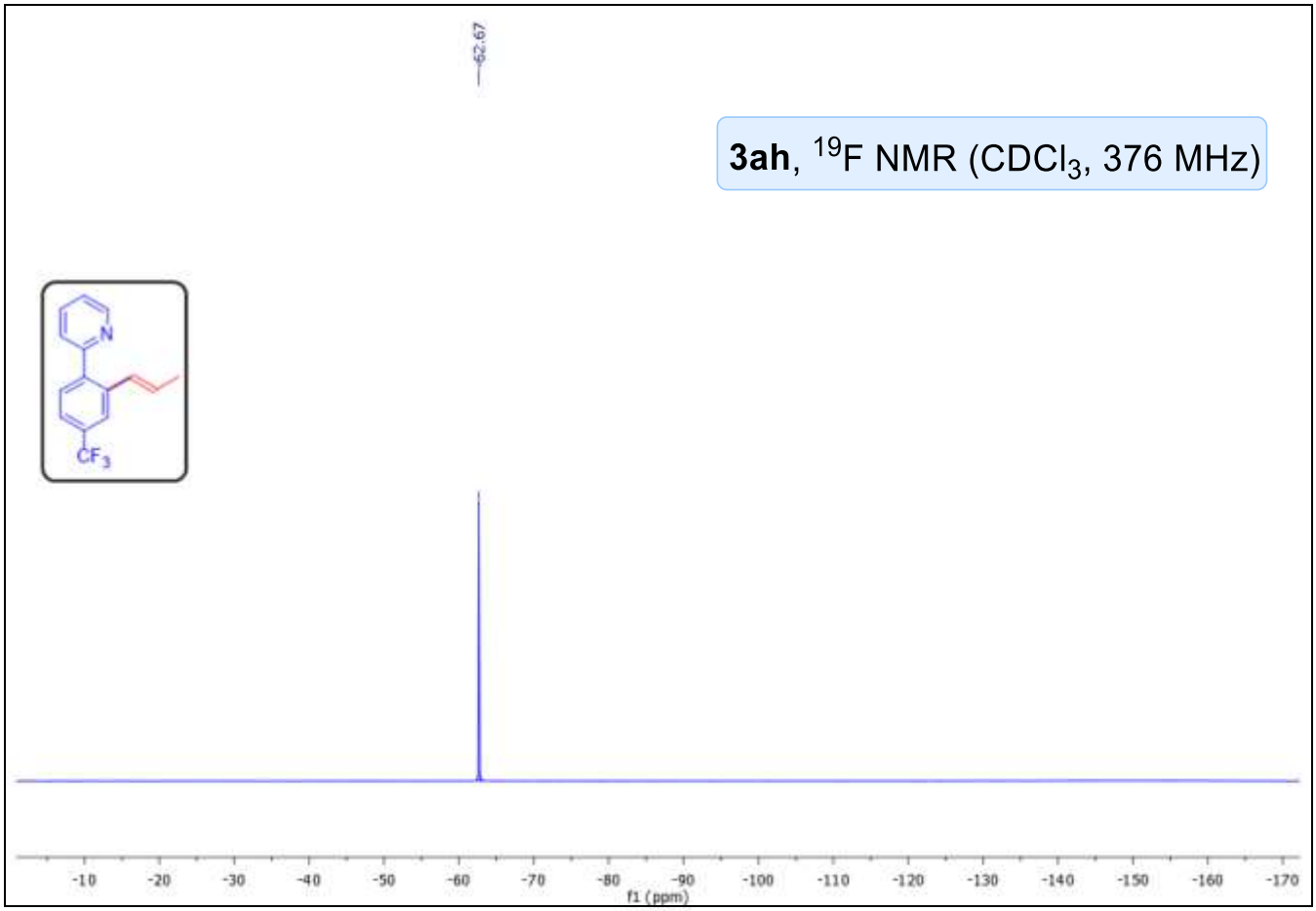




Bruker Compass DataAnalysis 4.0 printed: 2/25/2021 2:50:12 PM Page 1 of 1


8.746
8.734
7.815
7.776
7.771
7.564
7.550
7.547
7.440
7.420
7.309
6.493
6.458
6.454
6.325
6.308
6.292
6.275
6.269
6.253
1.856
1.852
1.840
1.836
0.000
3ah, 1H NMR (CDCl3, 400 MHz)
N
CF3
1.00
2.08
2.01
1.02
1.06
1.01
1.05
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


158.231
149.988
141.993
137.283
136.477
130.883
129.519
128.770
128.523
126.390
125.167
123.689
123.652
123.615
123.576
123.554
123.515
123.477
123.440
123.179
122.650
77.678
77.360
77.043
19.040
3ah, 13C{1H} NMR (CDCl3, 100 MHz)
N
CF3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.67
3ah, 19F NMR (CDCl3, 376 MHz)
N
CF3
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

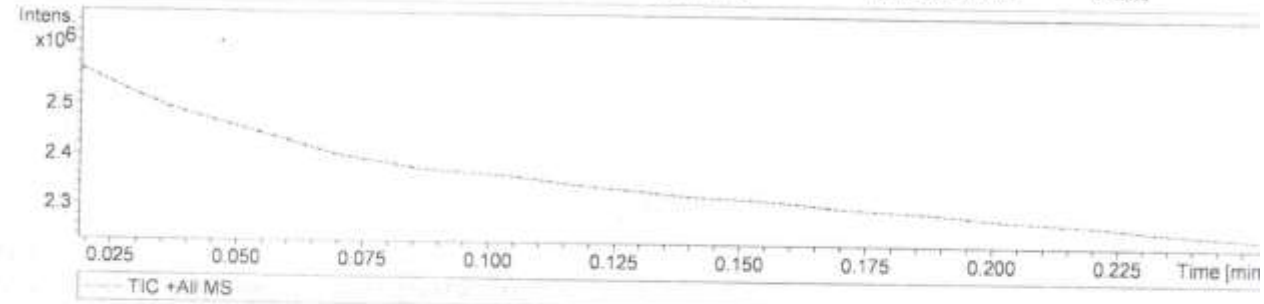
Display Report

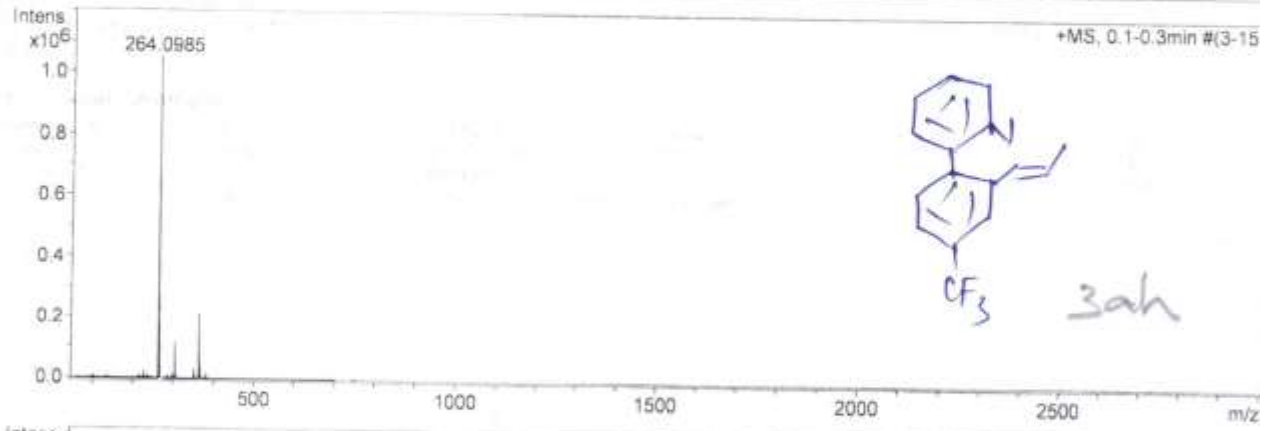
Analysis Info

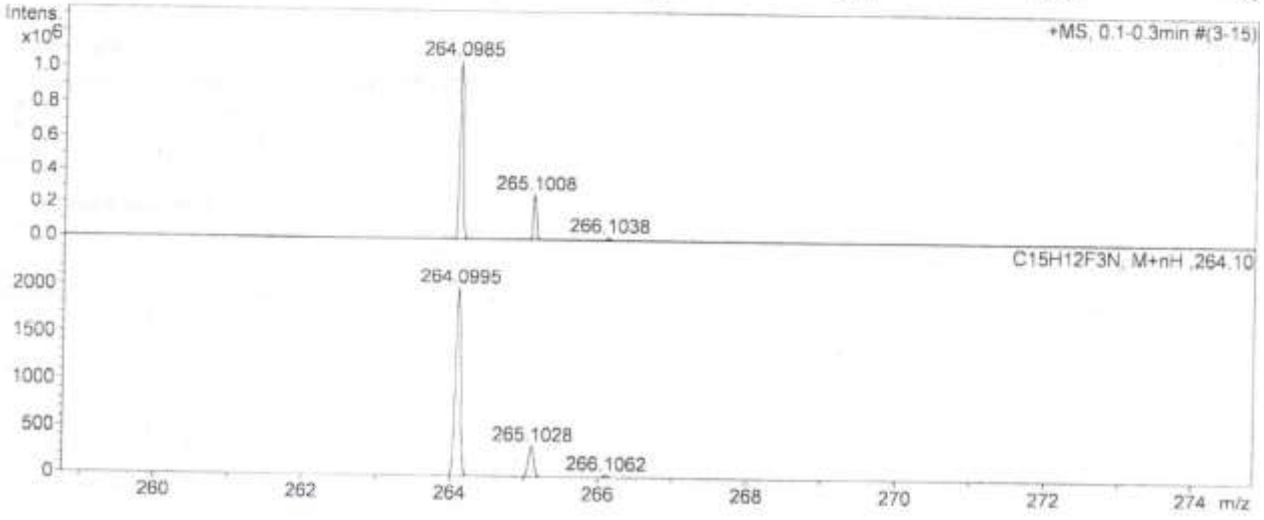
Analysis Name	D:\Data\FEB-2021\PCR\25022021_PCR_TN_1482.d	Acquisition Date	2/25/2021 2:44:09 PM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	PRAKASH BEHERA
Comment		Instrument	micrOTOF-Q II 10337

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







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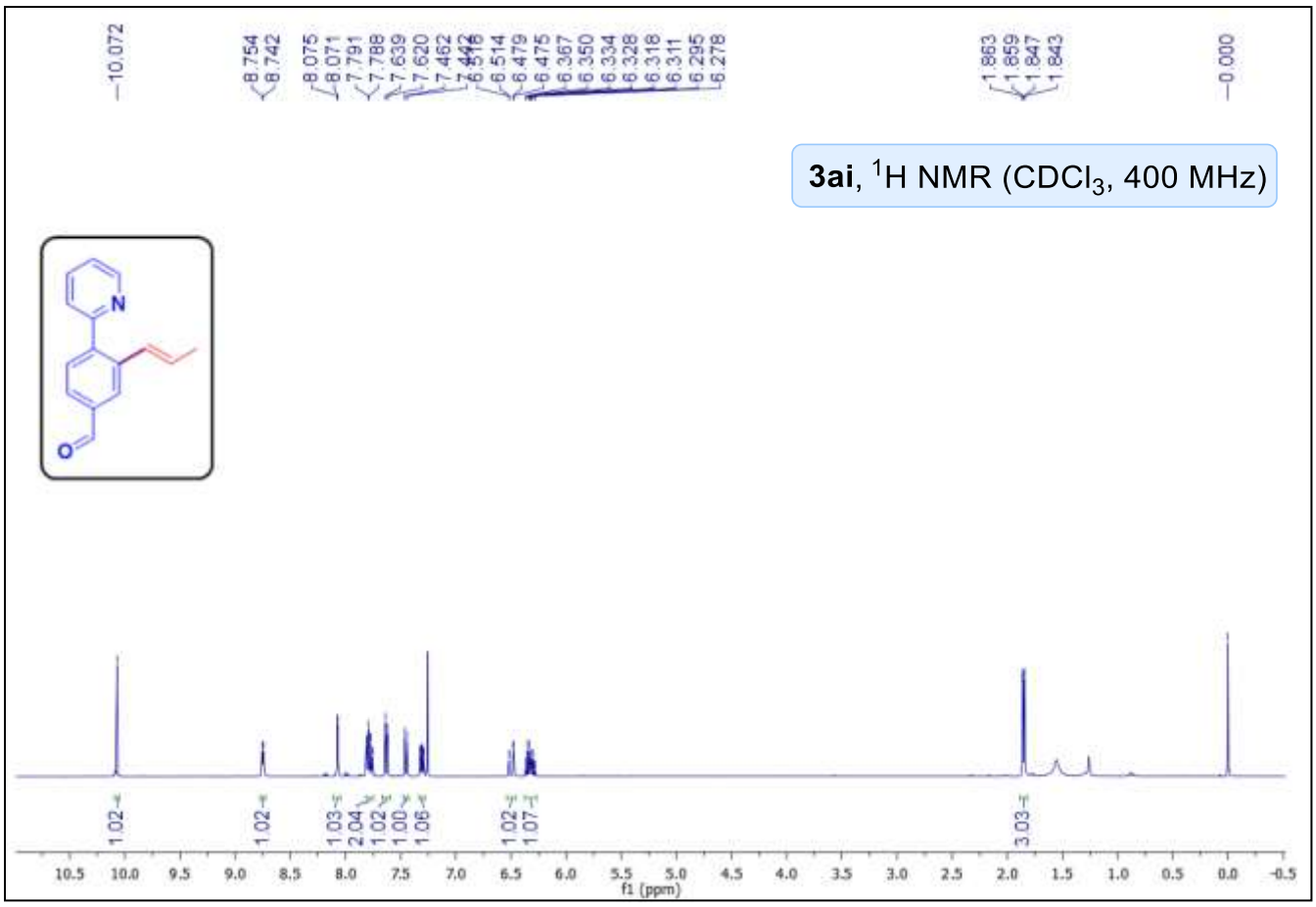
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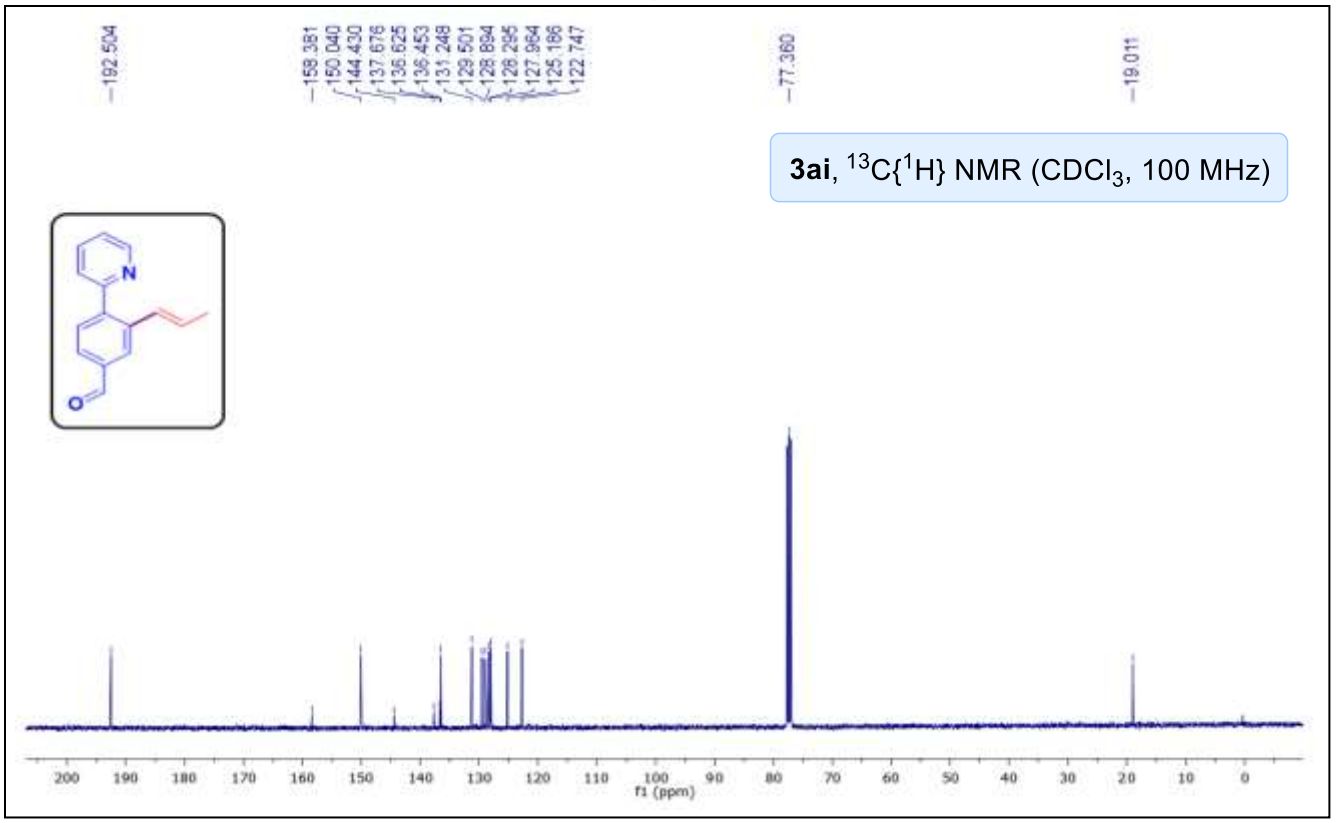
8.754
8.742
8.075
8.071
7.791
7.788
7.639
7.620
7.462
7.442
6.514
6.479
6.475
6.367
6.350
6.334
6.328
6.318
6.311
6.295
6.278
1.863
1.859
1.847
1.843
0.000
3ai, 1H NMR (CDCl3, 400 MHz)
1.02
1.02
1.03
2.04
1.02
1.00
1.06
1.02
1.07
3.03
f1 (ppm)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159.381
150.040
144.430
137.676
136.625
136.453
131.248
129.501
128.894
126.295
127.964
125.166
122.747
77.360
19.011
3ai, 13C{1H} NMR (CDCl3, 100 MHz)
f1 (ppm)

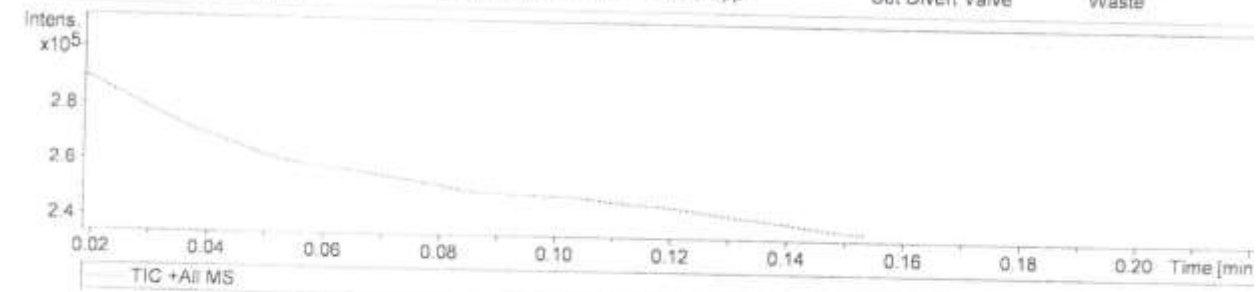
Display Report

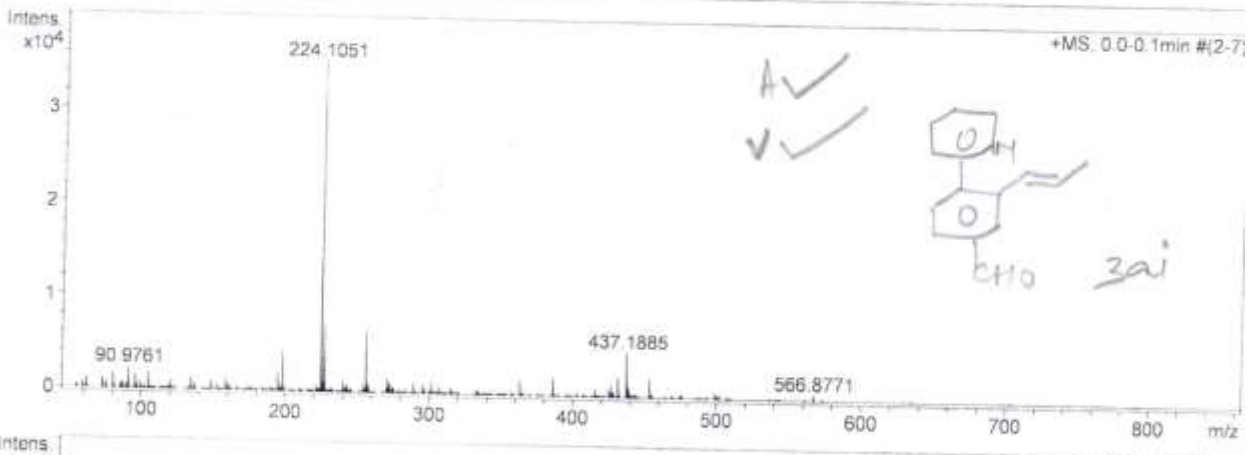
Analysis Info

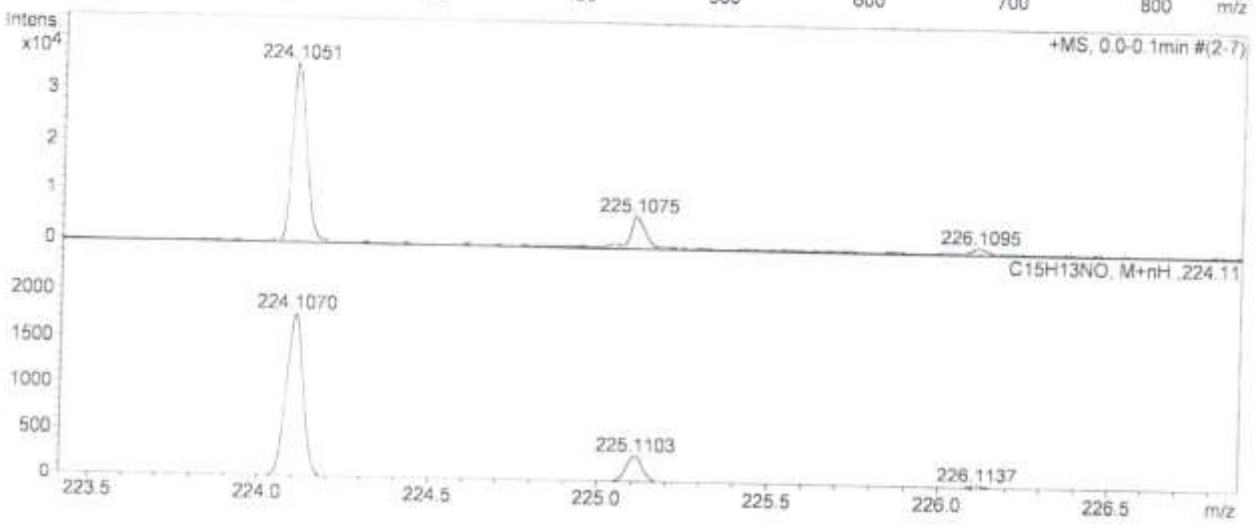
Analysis Name	D:\Data\MAR-2021\SN\23032021_SN_NS_1845.d	Acquisition Date	3/23/2021 3:37:39 PM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	Amit S.Sahu
Comment		Instrument	micrOTOF-Q II 10337

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







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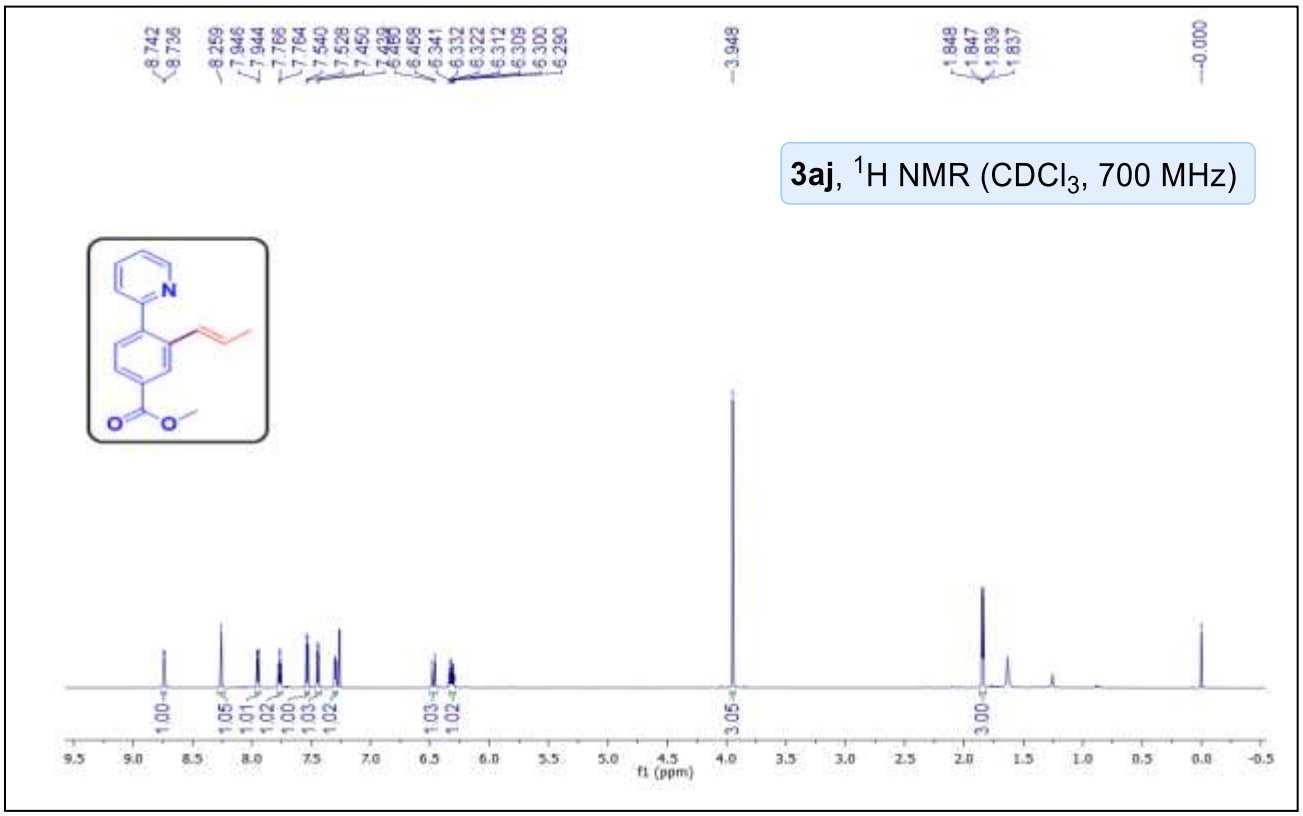
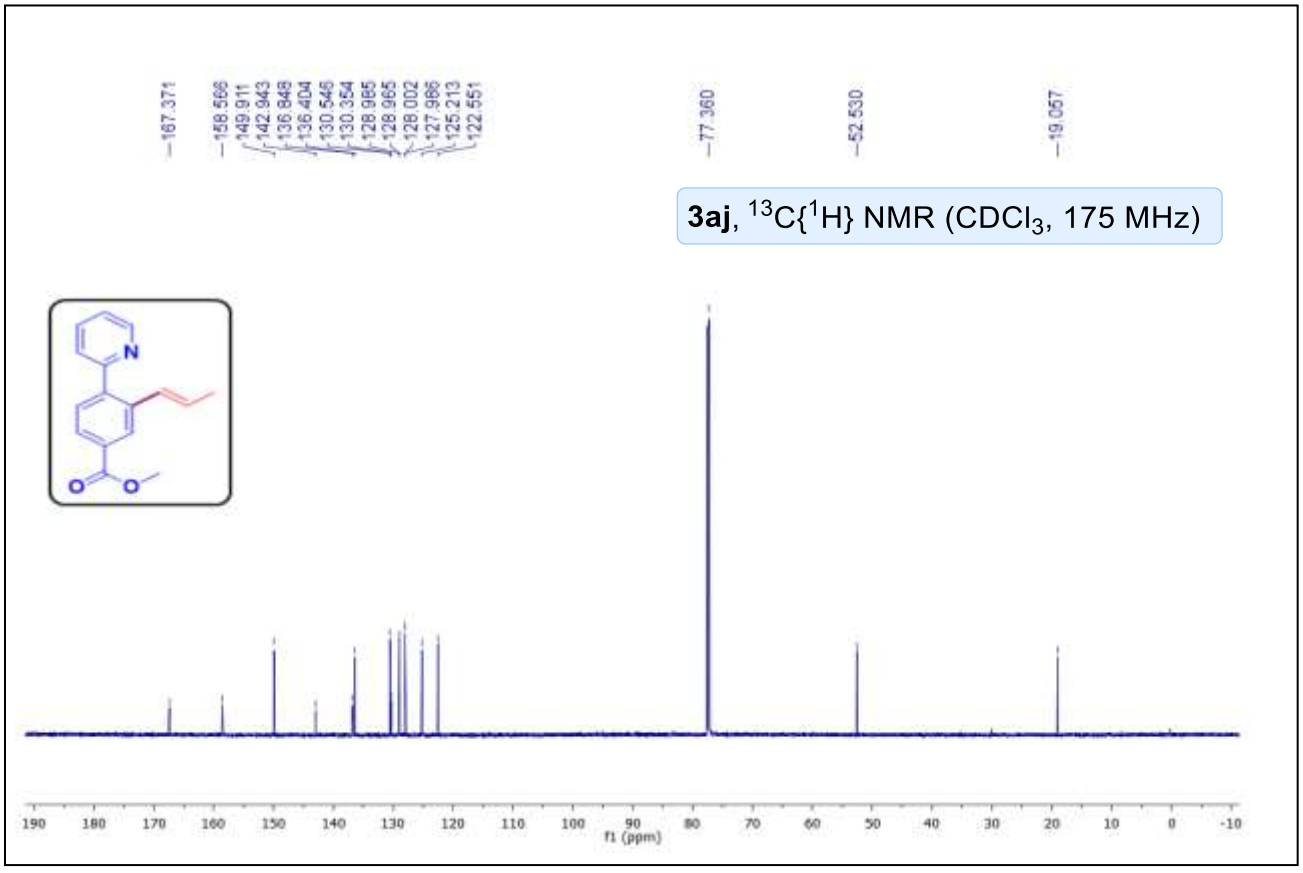


3aj, ^{1}H NMR ($CDCl_3$, 700 MHz)



3aj, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 175 MHz)

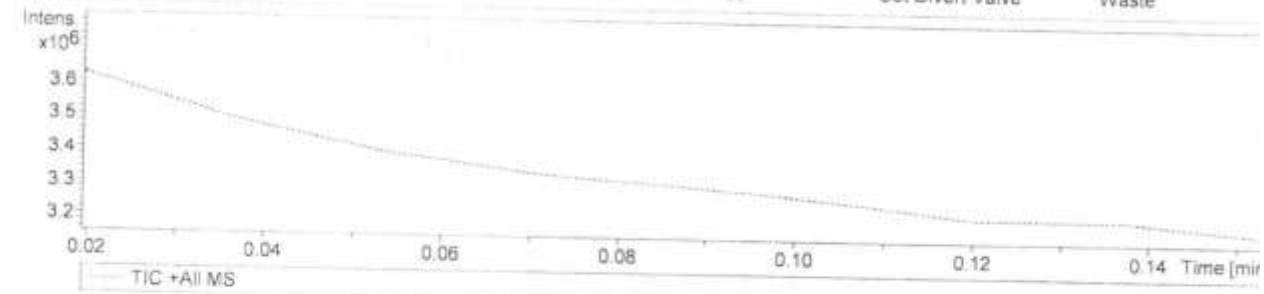
Display Report

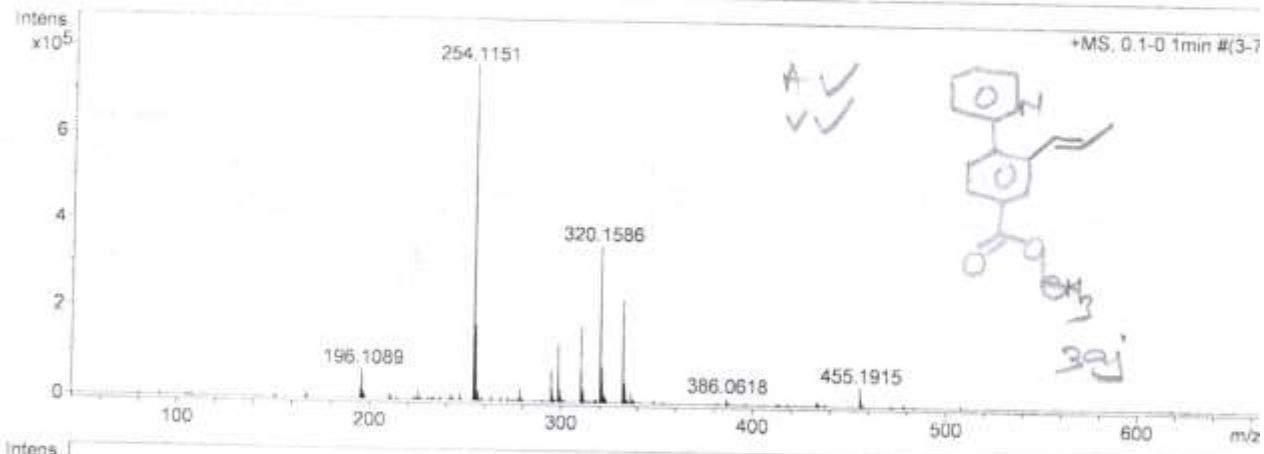
Analysis Info

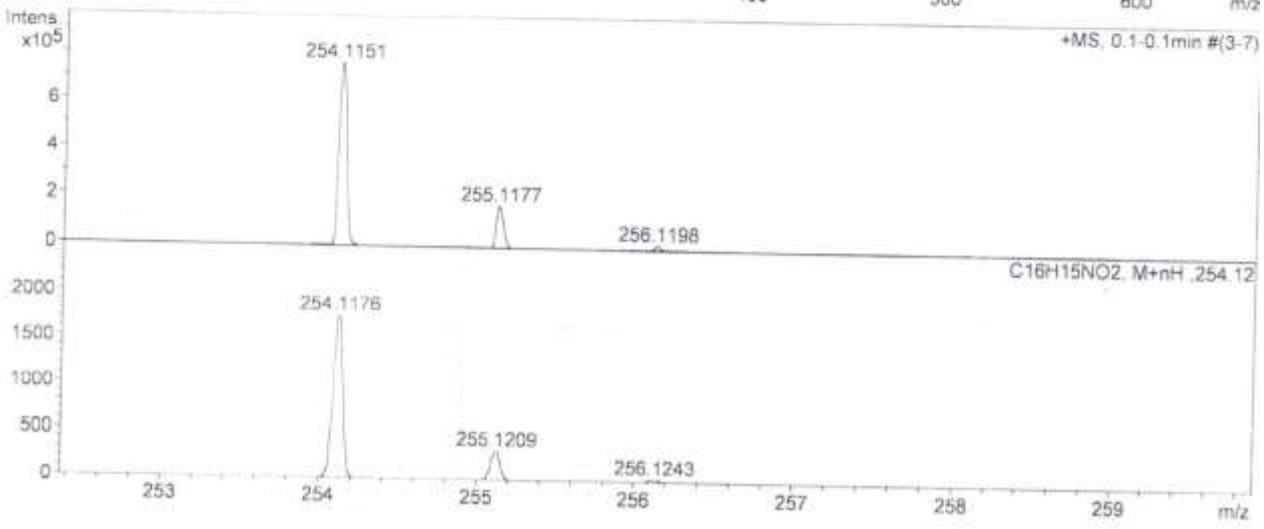
Analysis Name	D:\Data\MAR-2021\SN\24032021_SN_NS_1859.d	Acquisition Date	3/24/2021 12:05:23 PM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	Amit S.Sahu
Comment		Instrument	micrOTOF-Q II 10337

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







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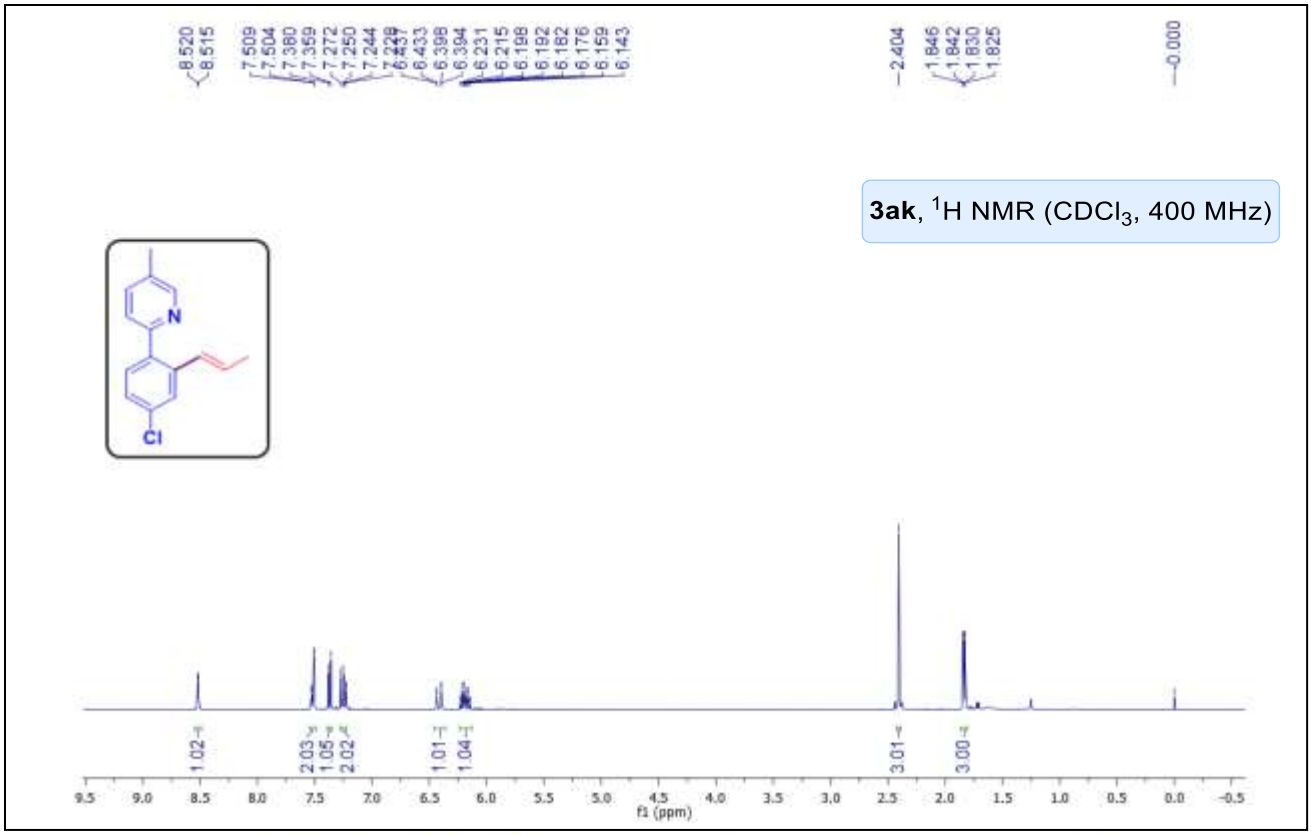
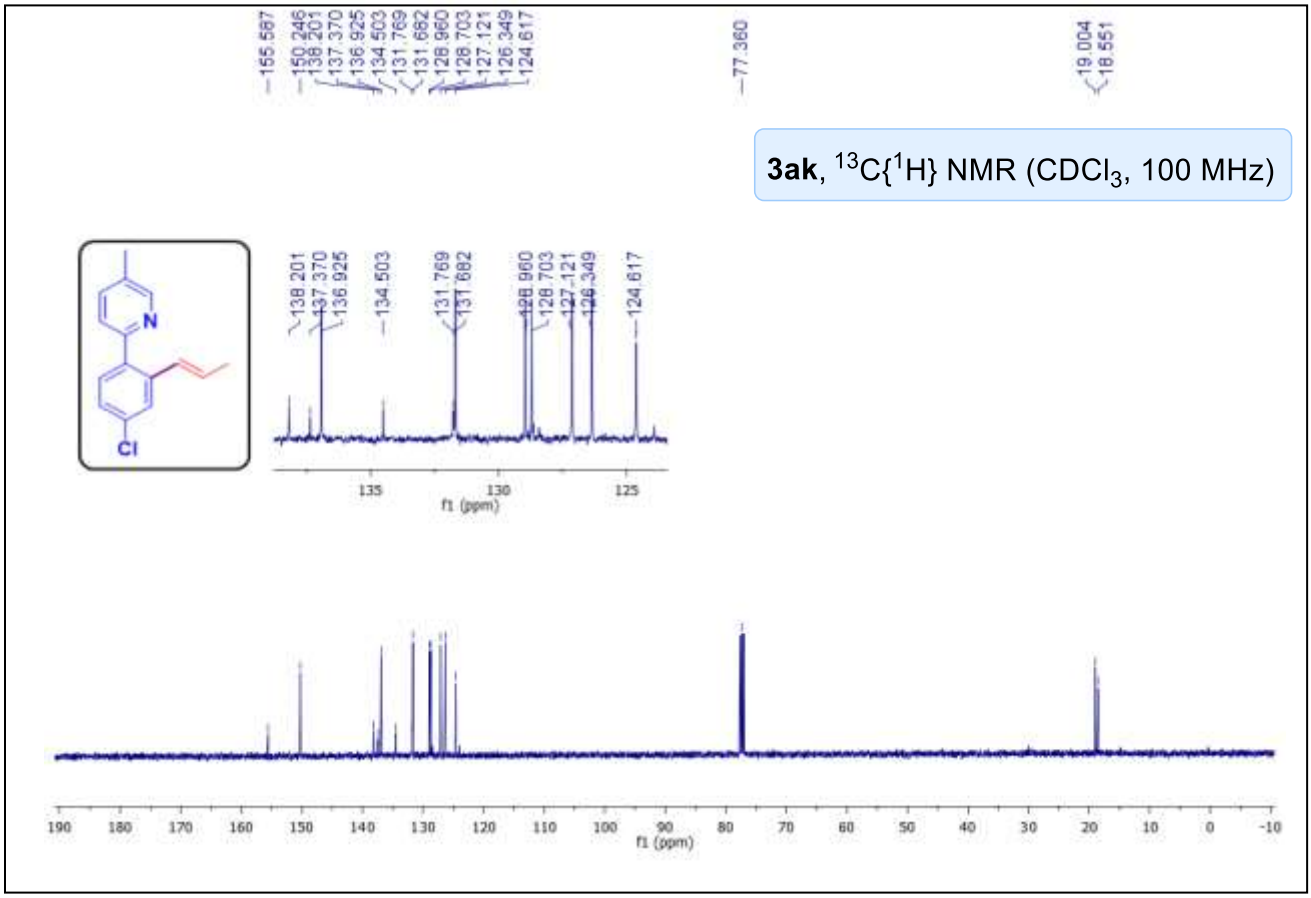


3ak, ^{1}H NMR ($CDCl_3$, 400 MHz)



3ak, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)

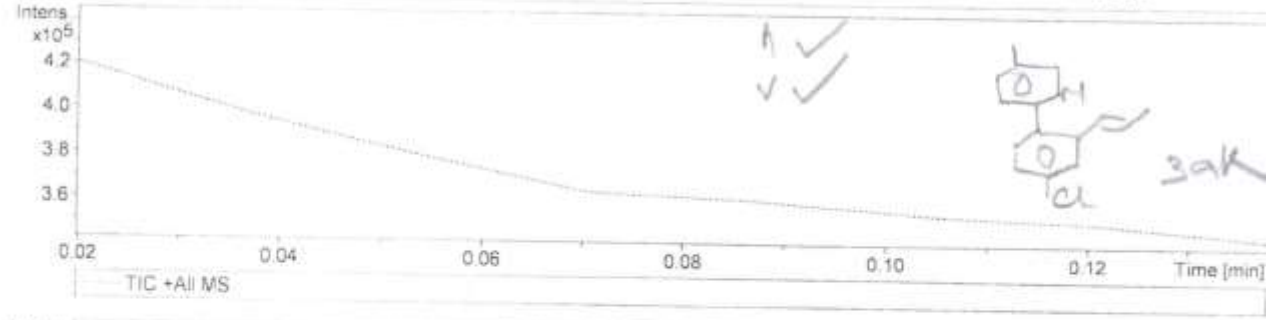
Display Report

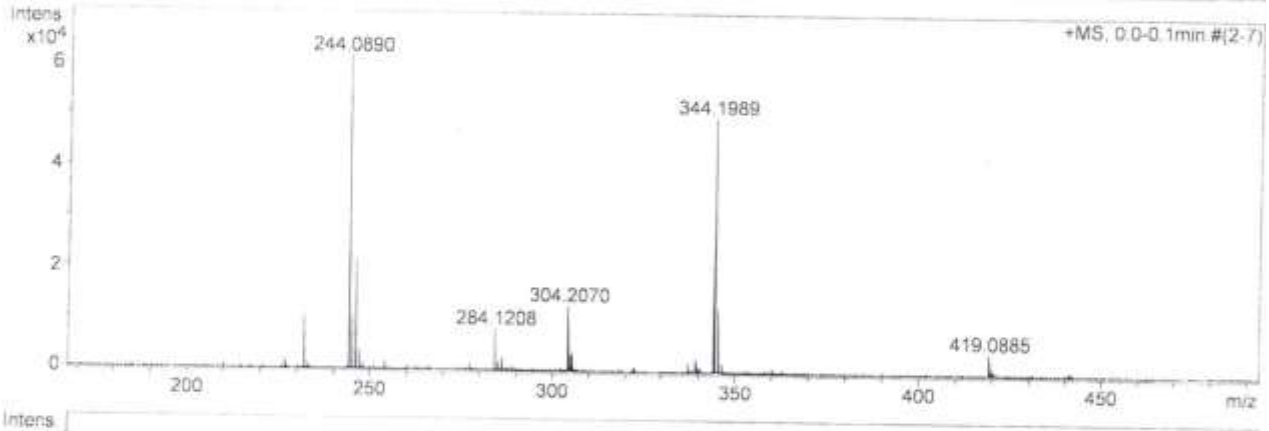
Analysis Info

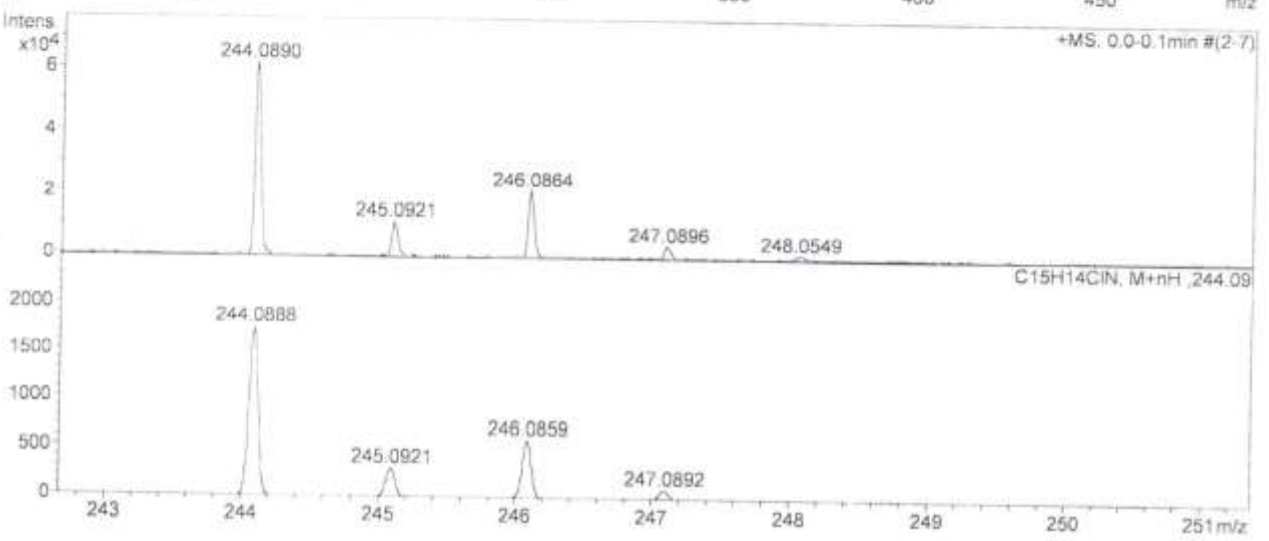
Analysis Name	D:\Data\MAR-2021\PCR\22032021_PCR_PB_1795.d	Acquisition Date	3/22/2021 10:55:13 AM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	Amit S.Sahu
Comment		Instrument	micrOTOF-Q II 10337

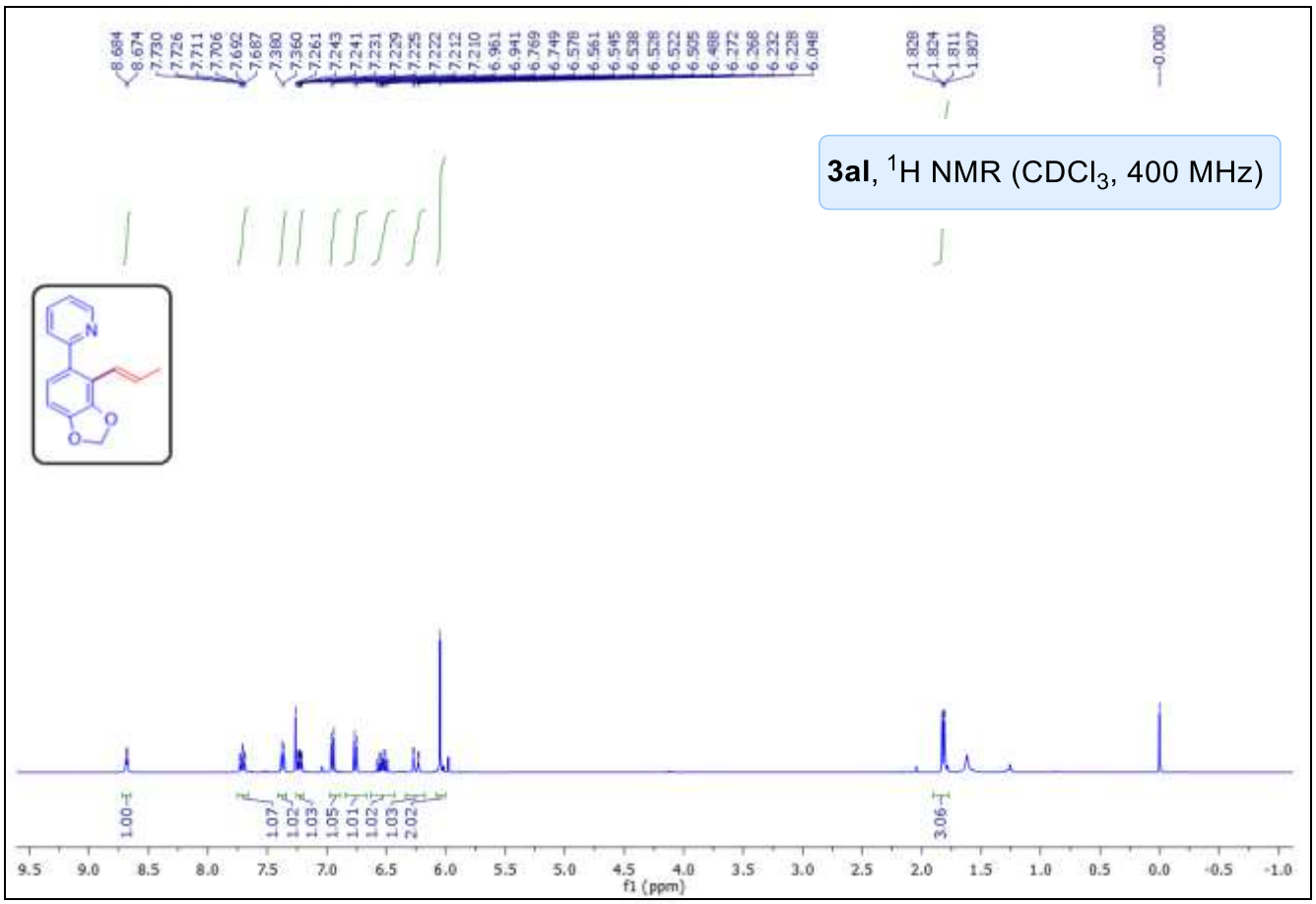
Acquisition Parameter

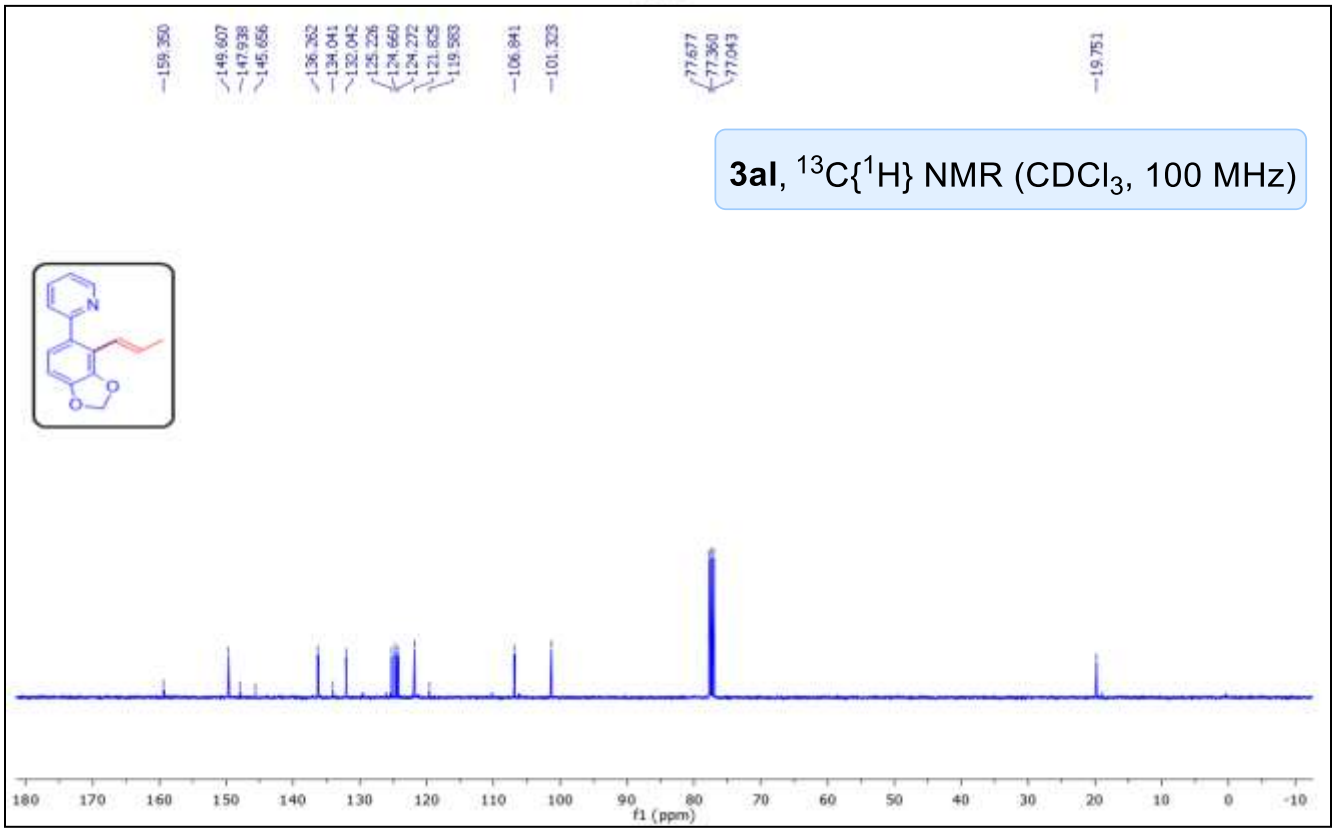
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








3al, 1H NMR (CDCl3, 400 MHz)
f1 (ppm)


3al, 13C{1H} NMR (CDCl3, 100 MHz)
f1 (ppm)

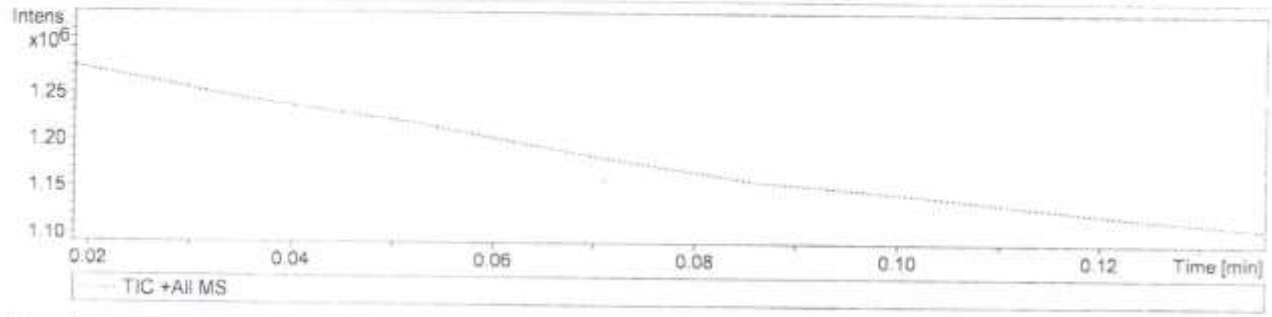
Display Report

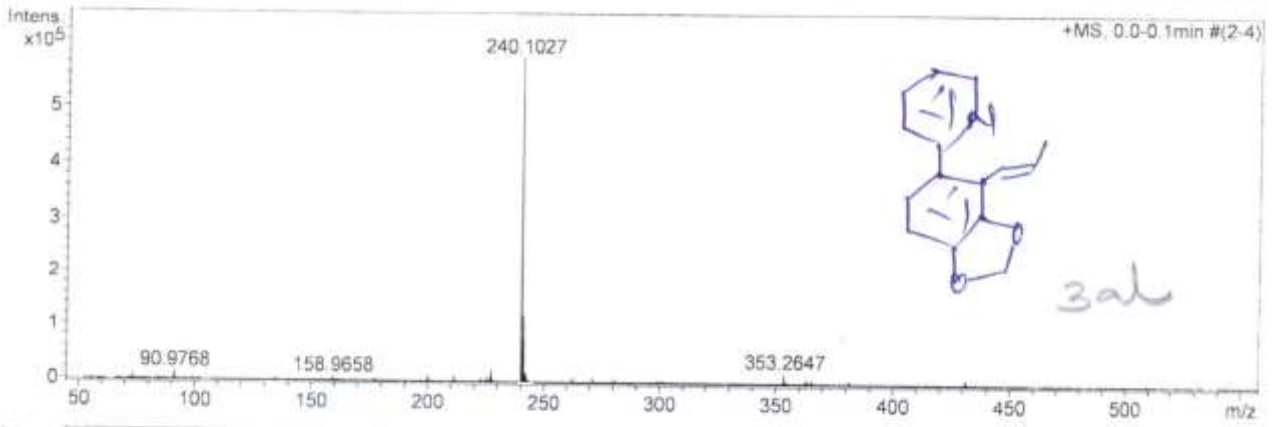
Analysis Info

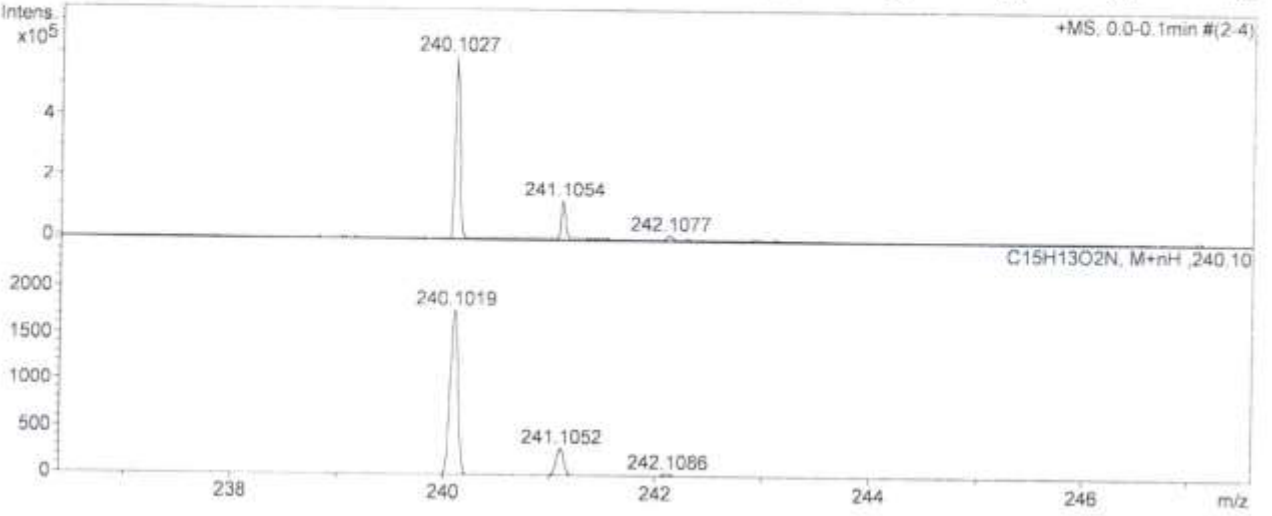
Analysis Name	D:\Data\FEB-2021\PCR\26022021_PCR_TN_1484.d	Acquisition Date	2/26/2021 11:31:15 AM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	Amit S.Sahu
Comment		Instrument	micrOTOF-Q II 10337

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







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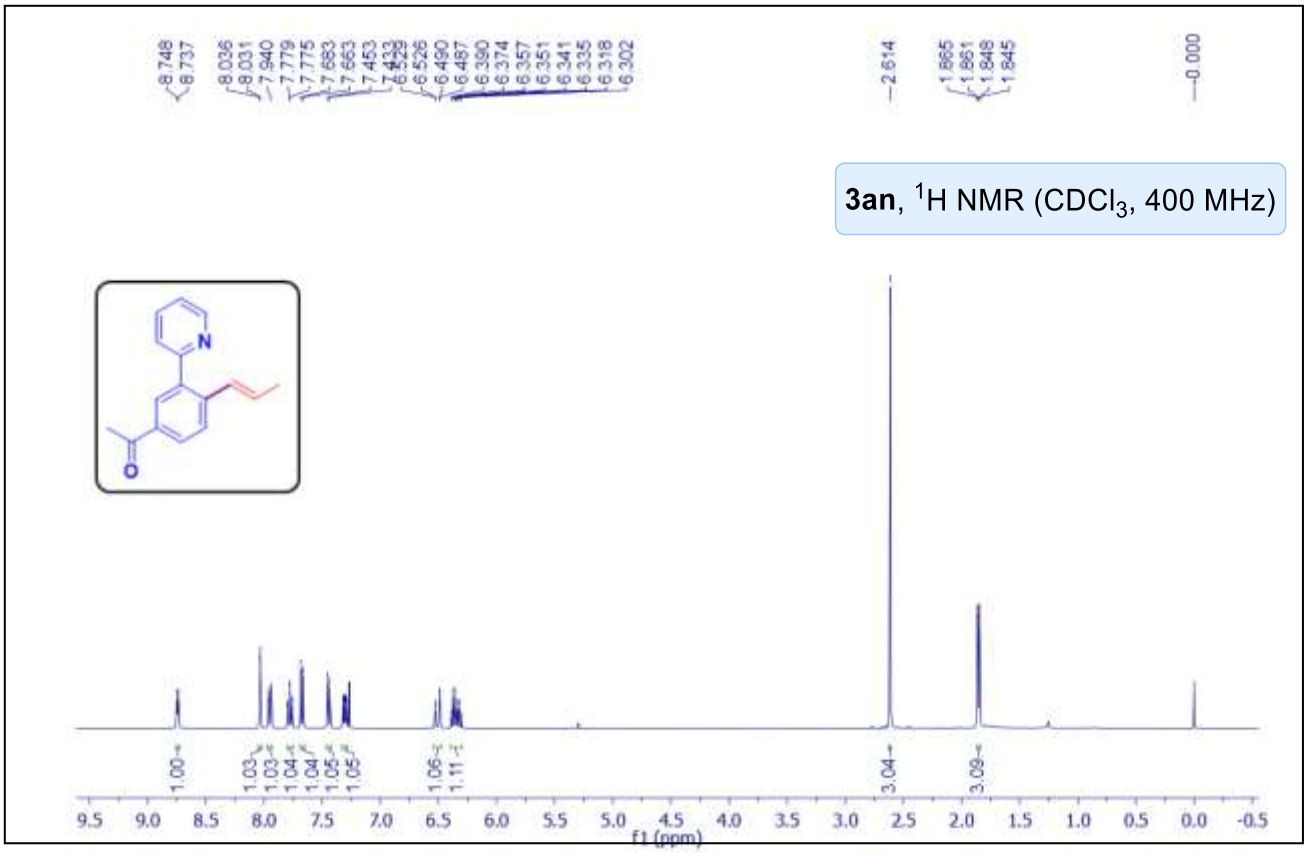
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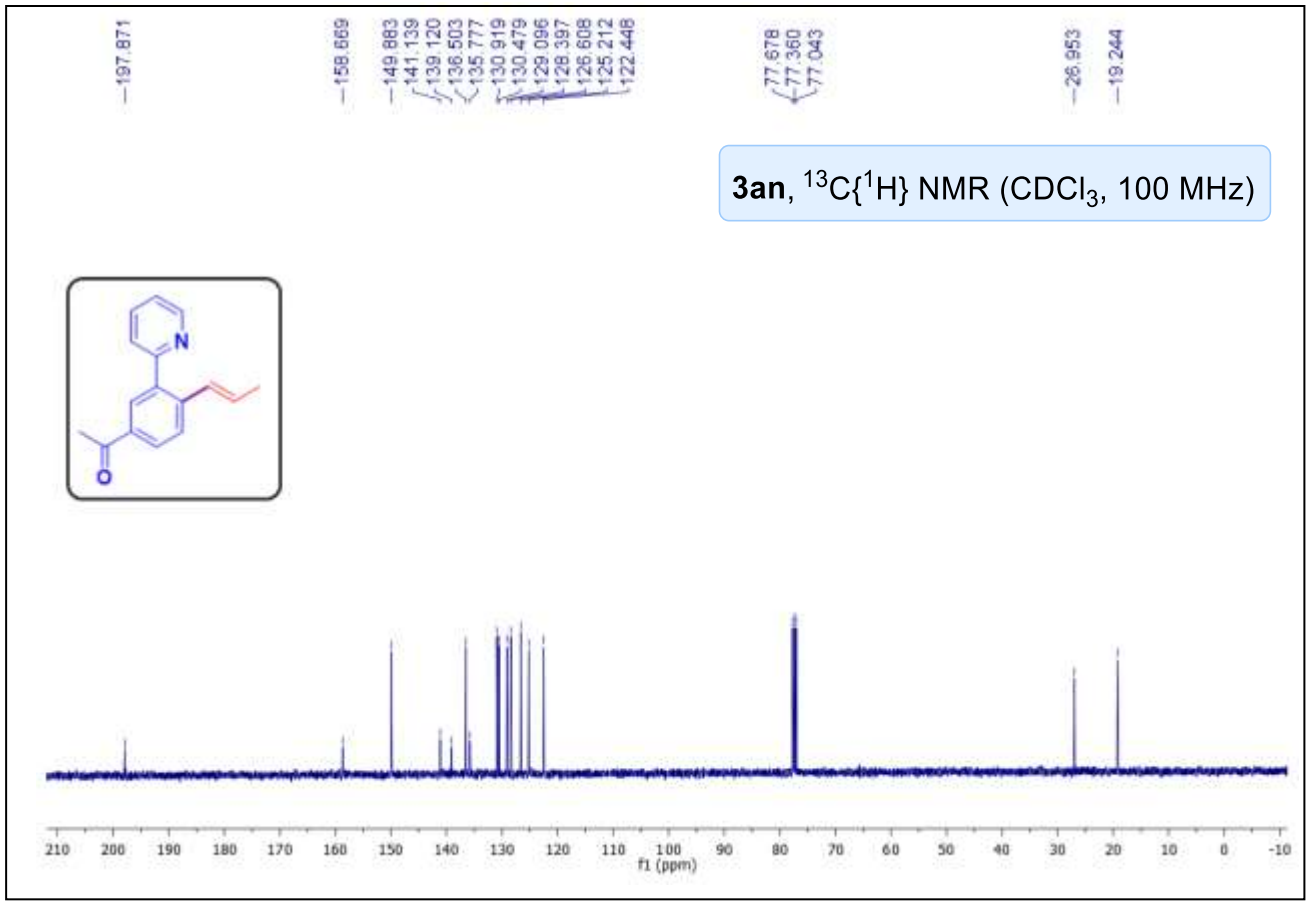
7.779
7.775
7.683
7.663
7.453
7.433
7.428
6.526
6.490
6.487
6.390
6.374
6.357
6.351
6.341
6.335
6.318
6.302
2.614
1.865
1.861
1.848
1.845
0.000
3an, 1H NMR (CDCl3, 400 MHz)
N
O
1.00
1.03
1.03
1.04
1.04
1.05
1.05
1.06
1.11
3.04
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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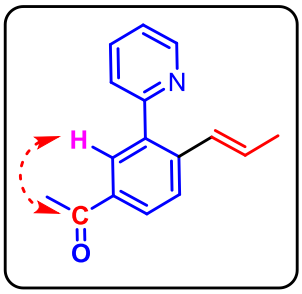
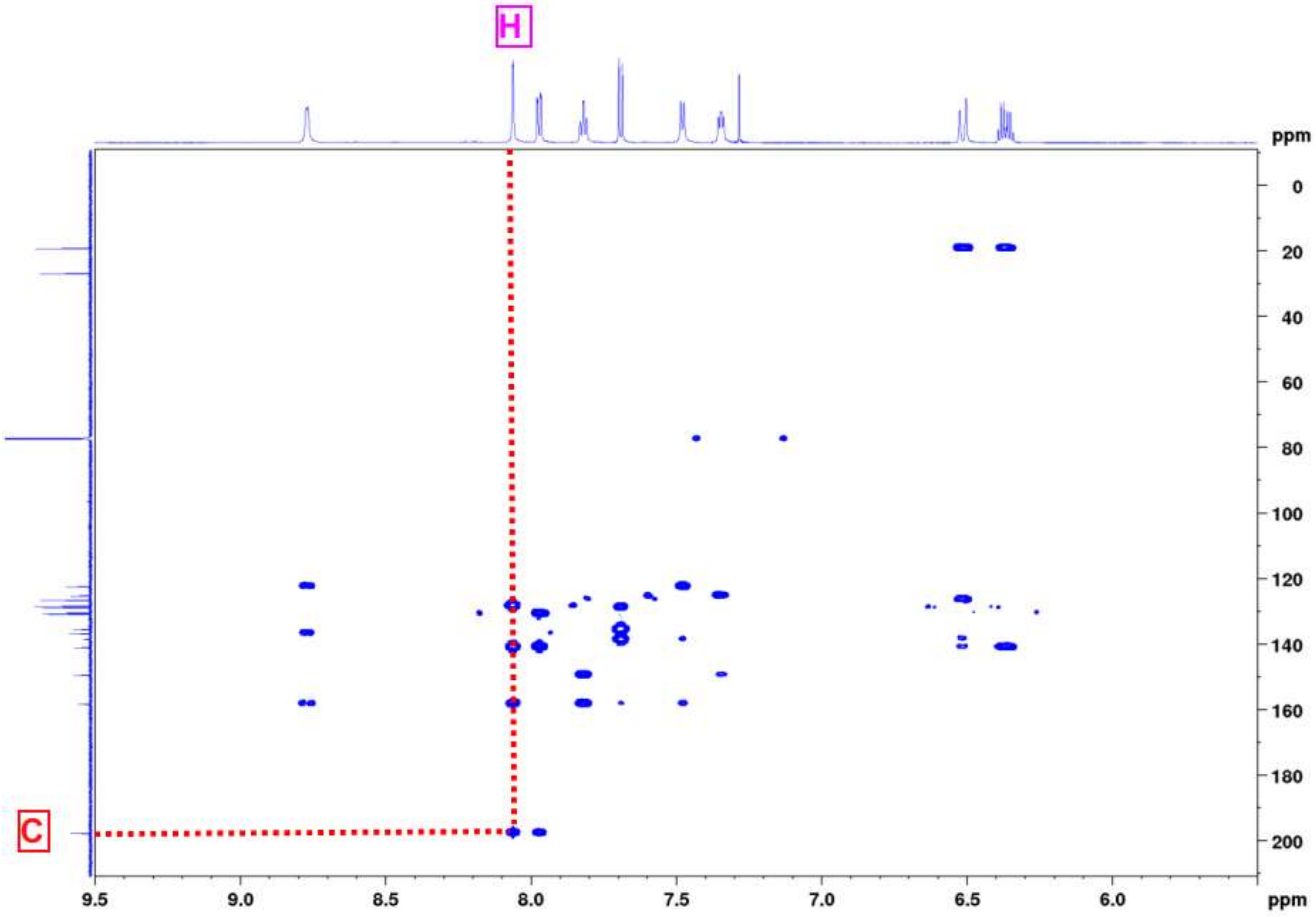
149.883
141.139
139.120
136.503
135.777
130.919
130.479
129.096
128.397
126.608
125.212
122.448
77.678
77.360
77.043
26.953
19.244
3an, 13C{1H} NMR (CDCl3, 100 MHz)
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{1}H-^{13}C HMBC spectrum of the product 3an.





Display Report

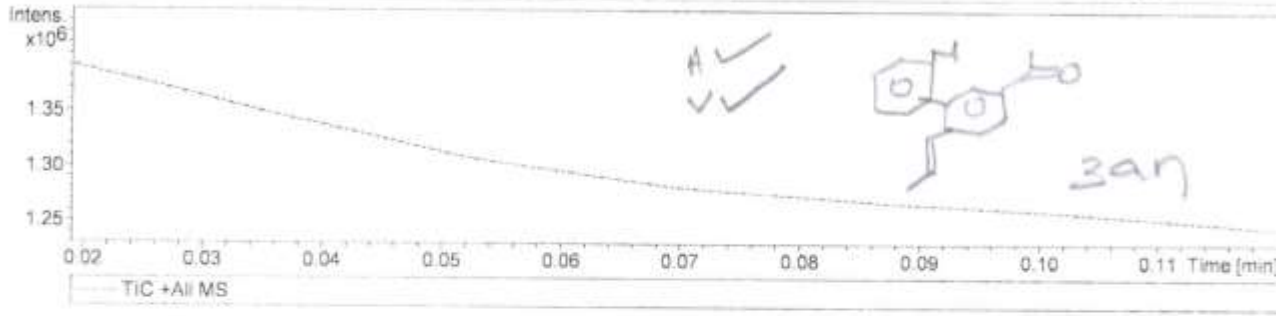
Analysis Info

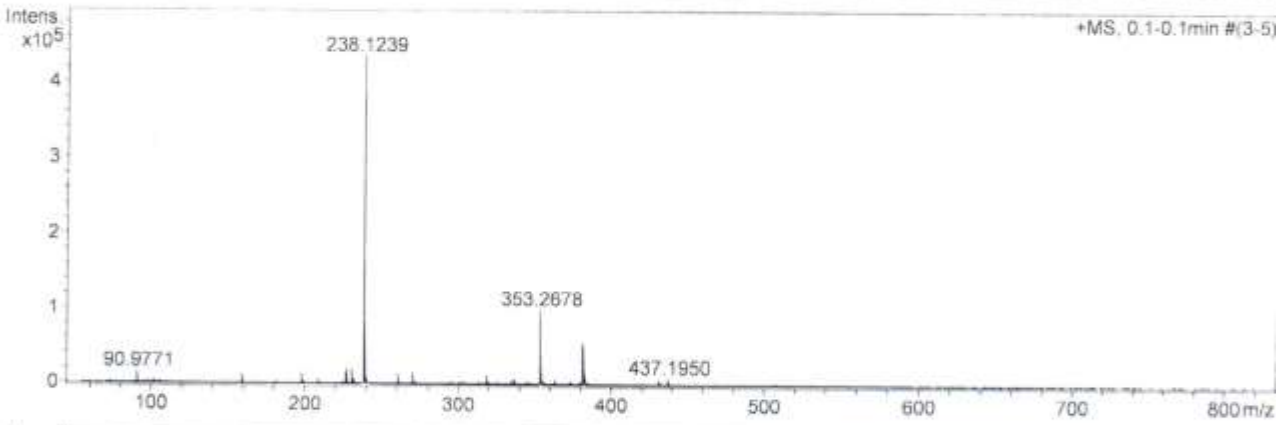
Analysis Name	D:\Data\FEB-2021\PCR\24022021_PCR_PB_1780.d	Acquisition Date	2/24/2021 3:16:11 PM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	Amit S.Sahu
Comment		Instrument	micrOTOF-Q II 10337

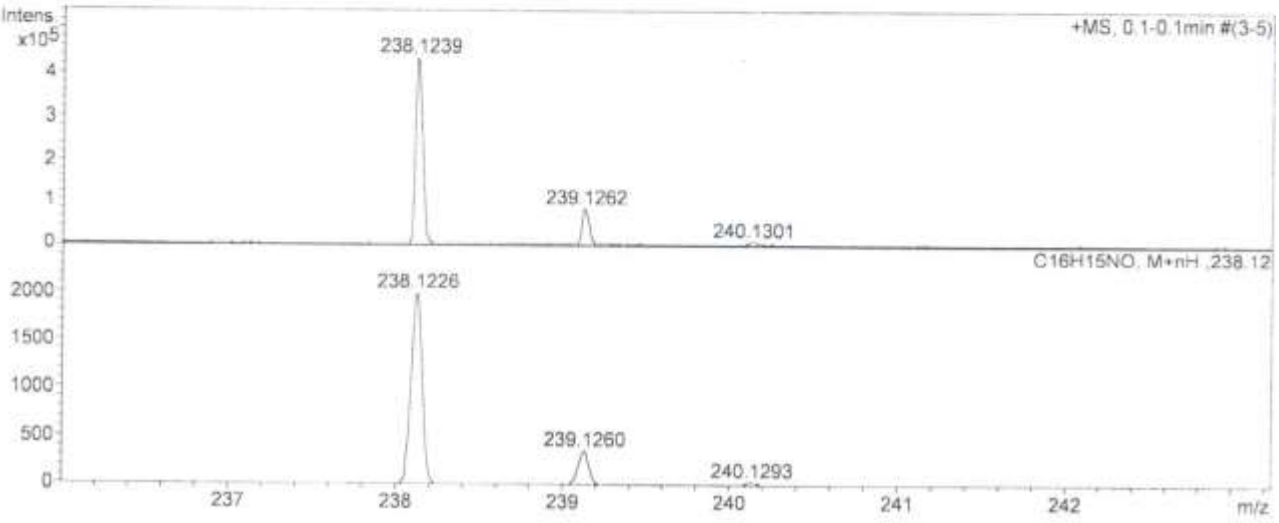
1803

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







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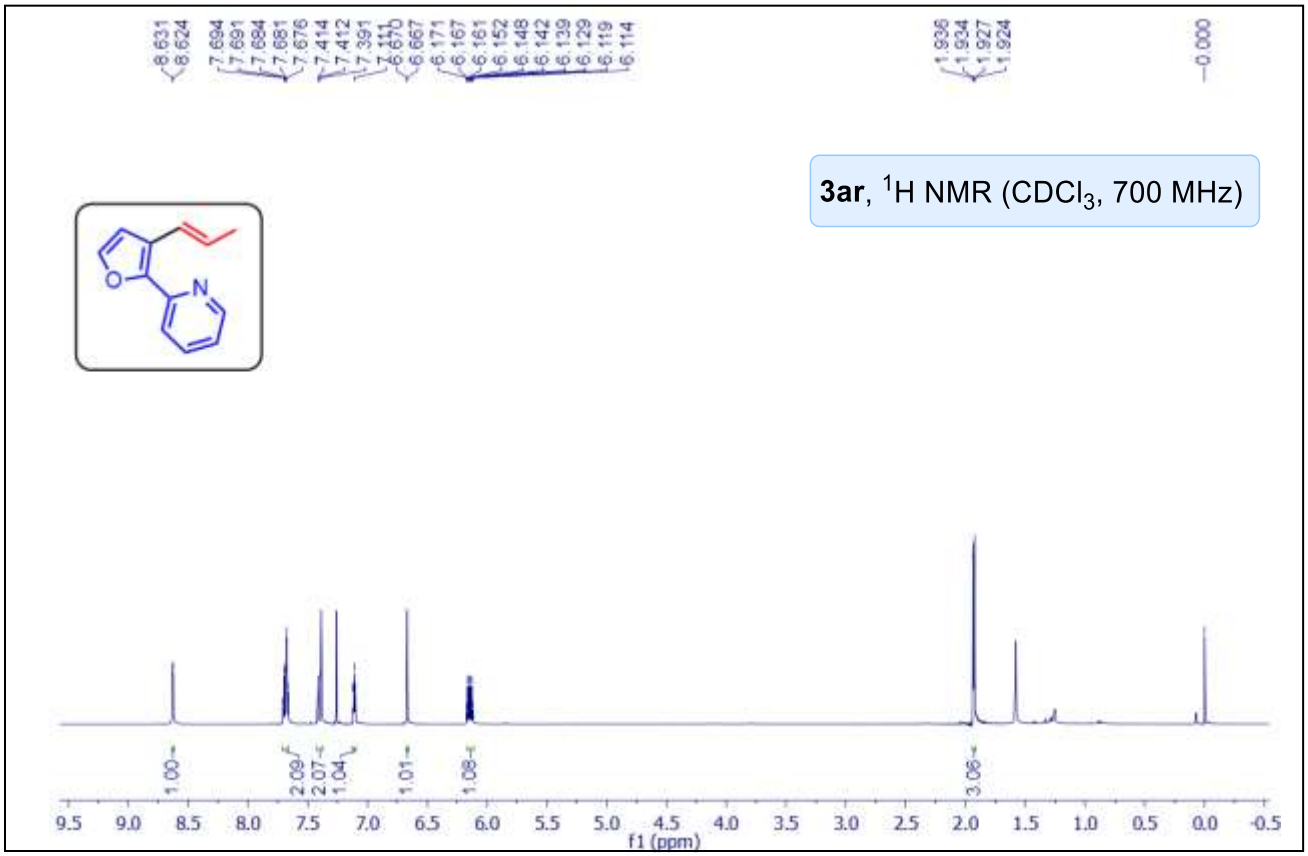
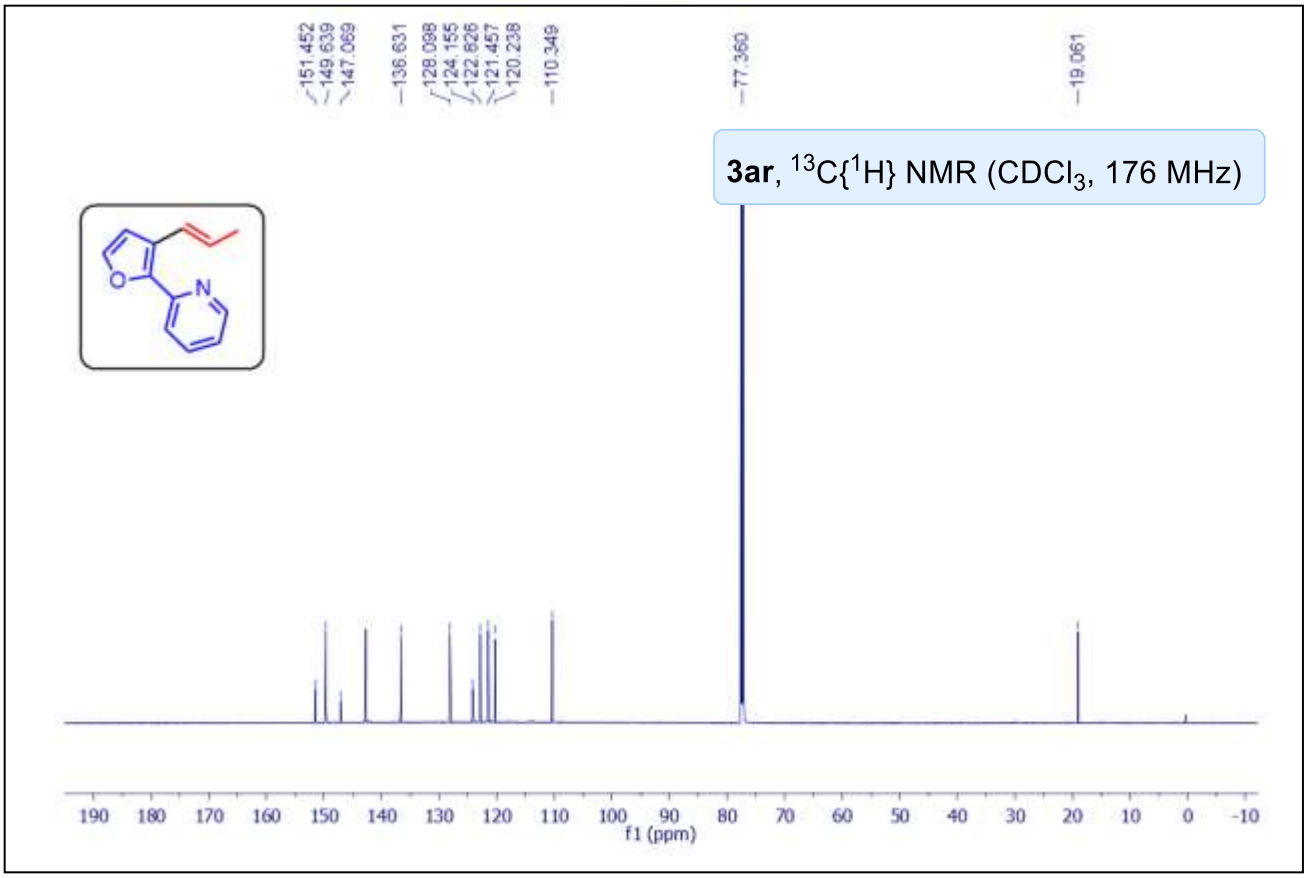


3ar, ^{1}H NMR ($CDCl_3$, 700 MHz)



3ar, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 176 MHz)

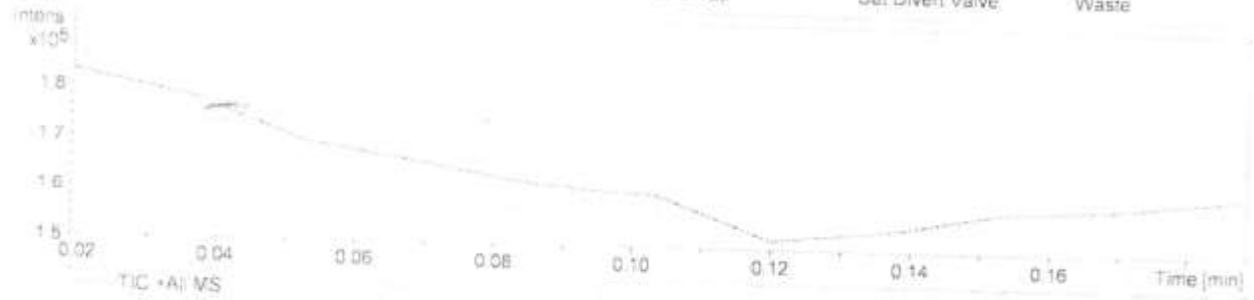
Display Report

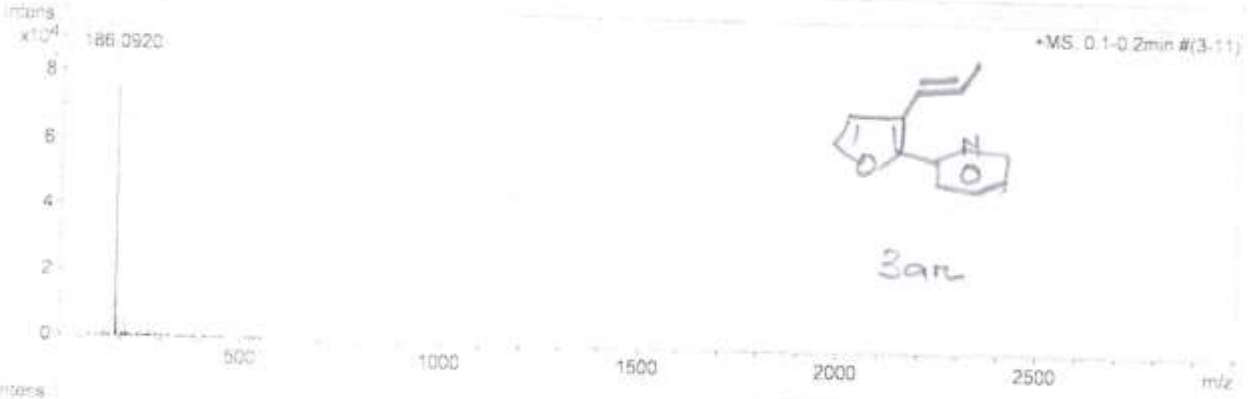
Analysis Info

Analysis Name	D:\Data\NOV-2021\PCR\30112021_PCR_TN_2134.d	Acquisition Date	11/30/2021 11:12:58 AM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	PRAKASH BEHERA
Comment		Instrument	micrOTOF-Q II 10337

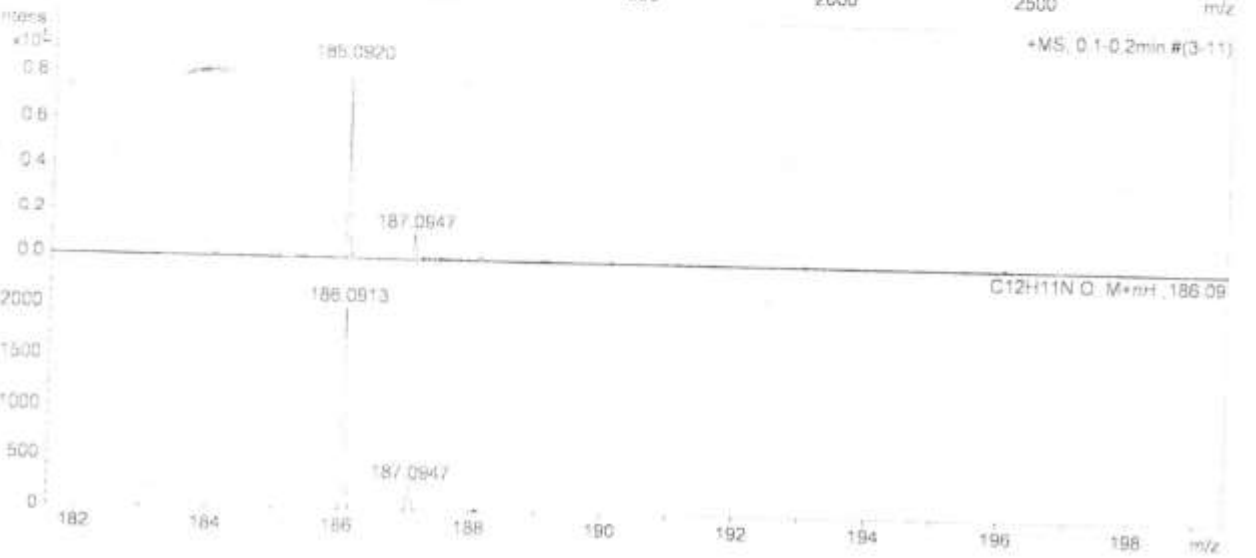
Acquisition Parameter

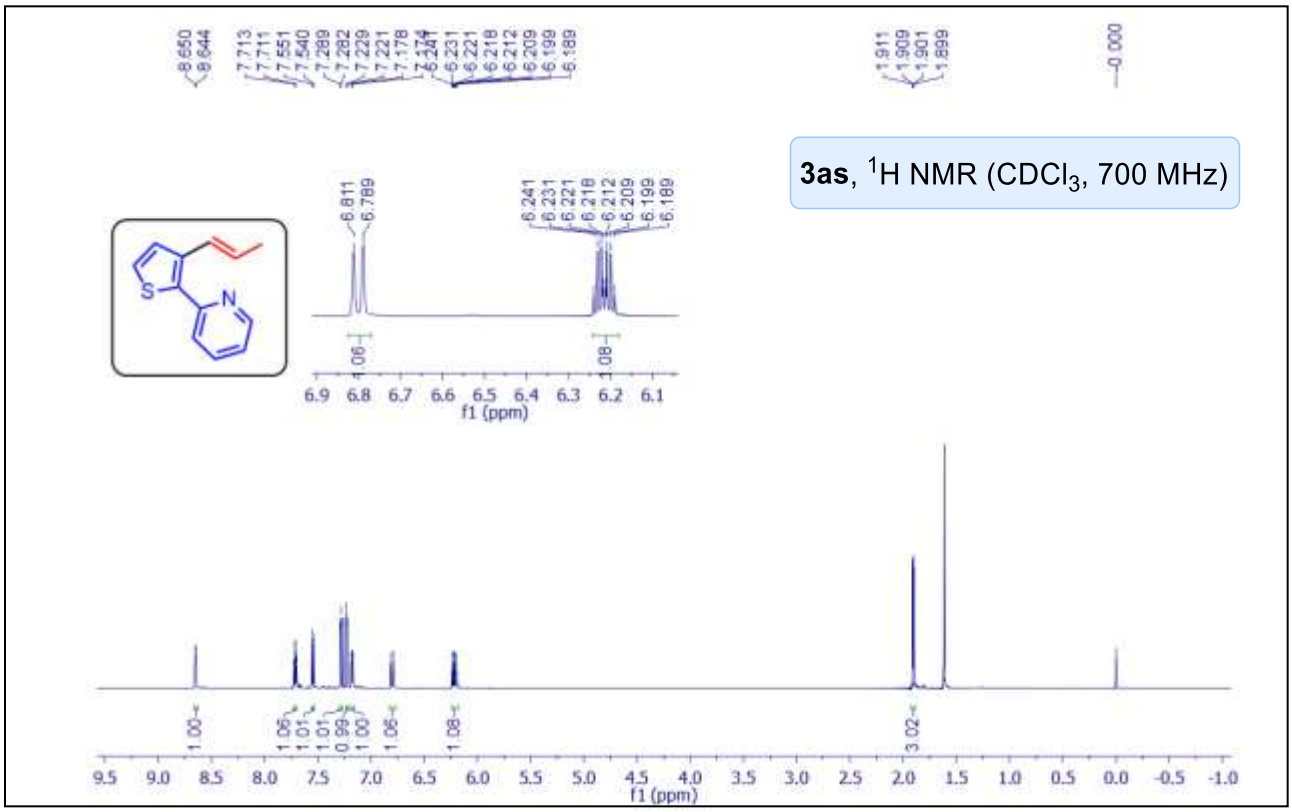
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



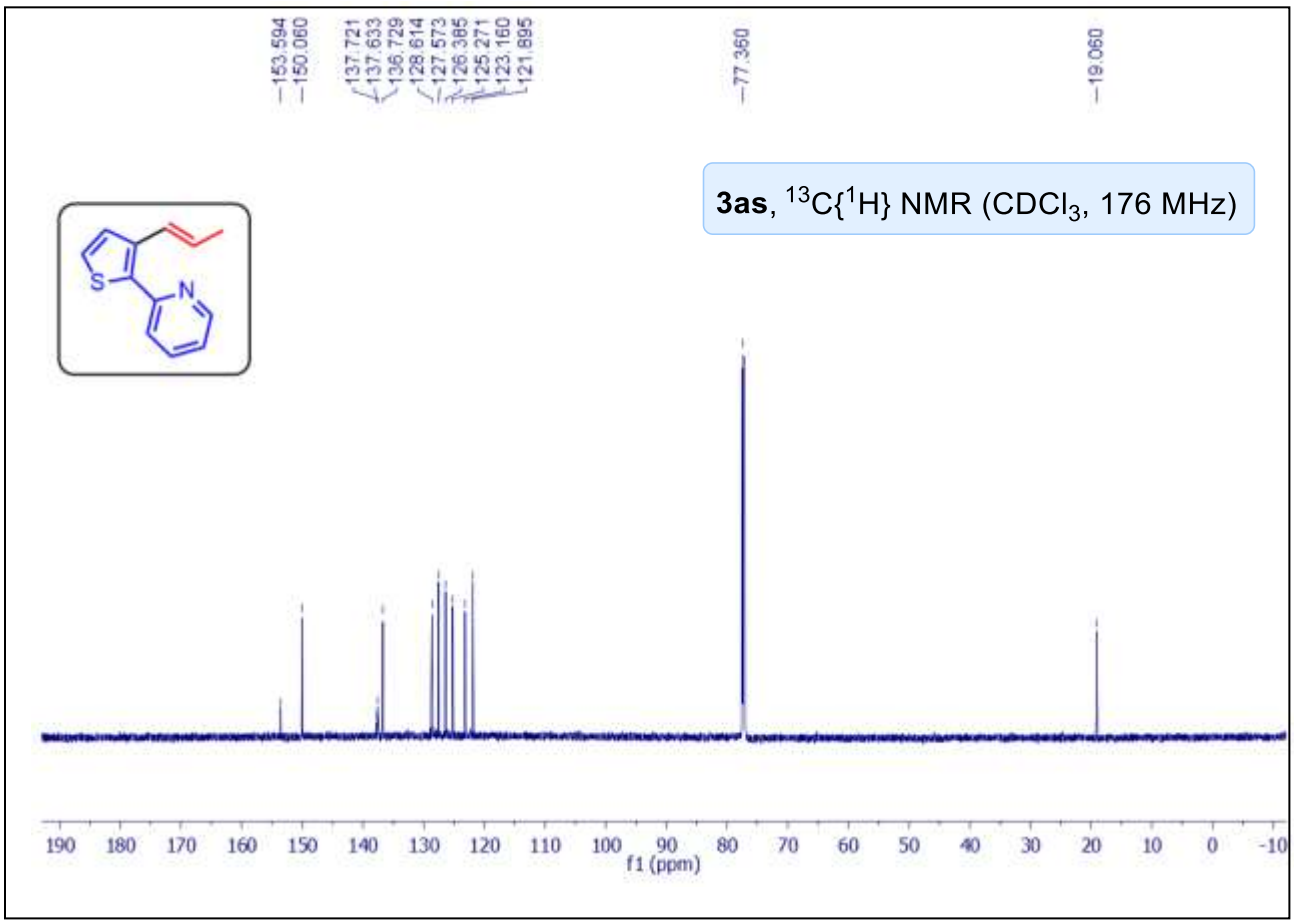


3an





3as, ^{1}H NMR ($CDCl_3$, 700 MHz)



3as, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 176 MHz)

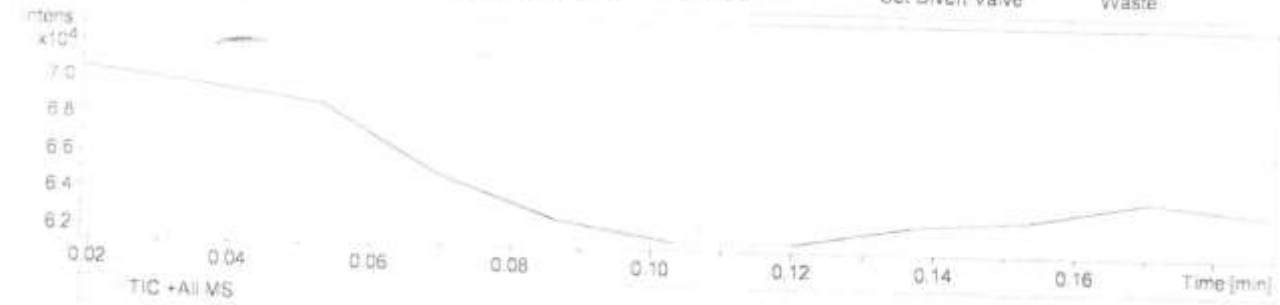
Display Report

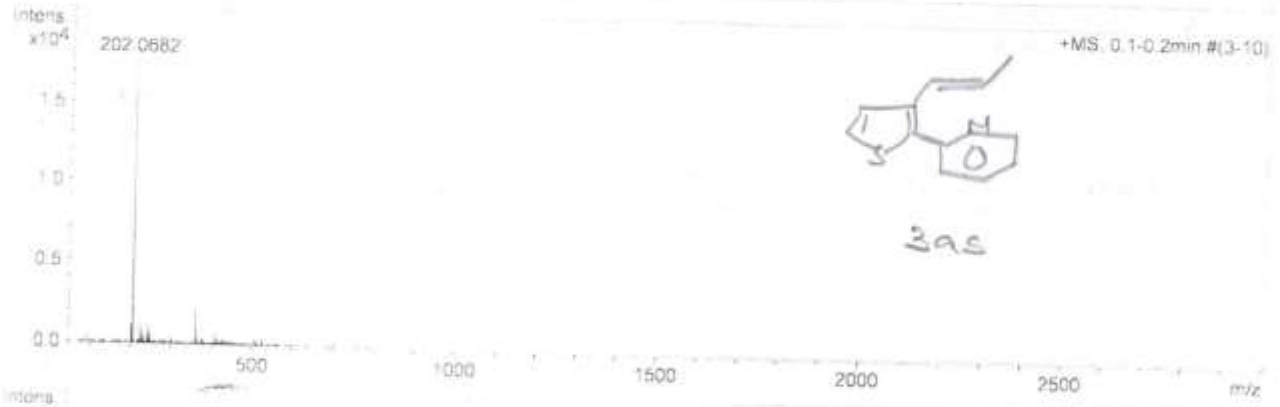
Analysis Info

Analysis Name	D:\Data\NOV-2021\PCR\30112021_PCR_TN_2133_R.d	Acquisition Date	11/30/2021 11:09:37 AM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	PRAKASH BEHERA
Comment		Instrument	micrOTOF-Q II 10337

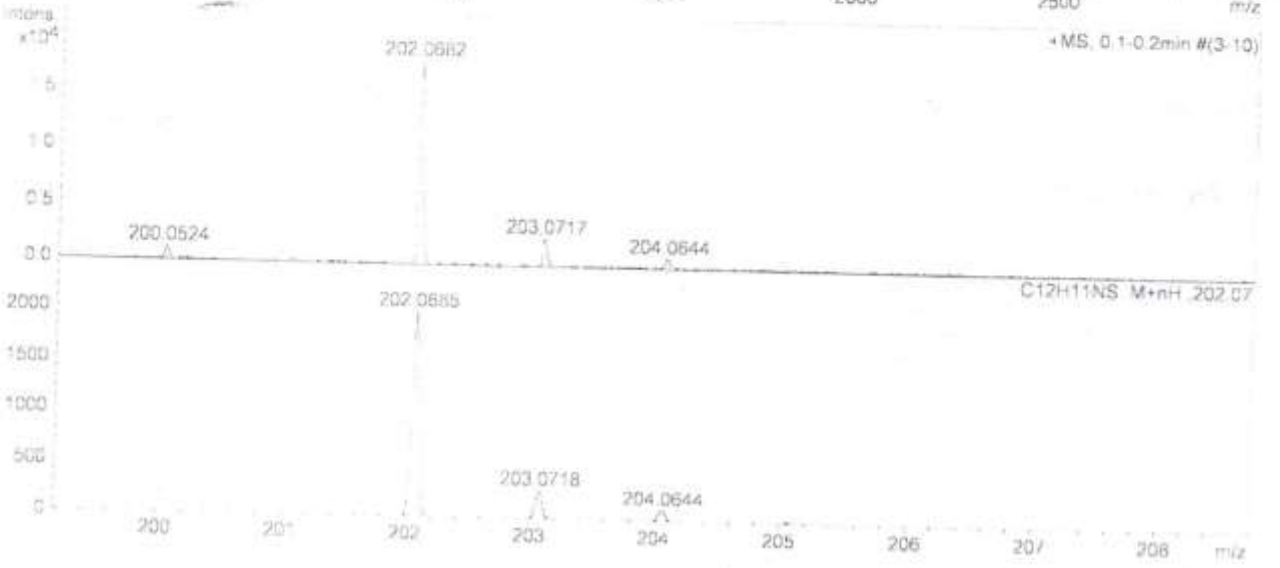
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste





3as



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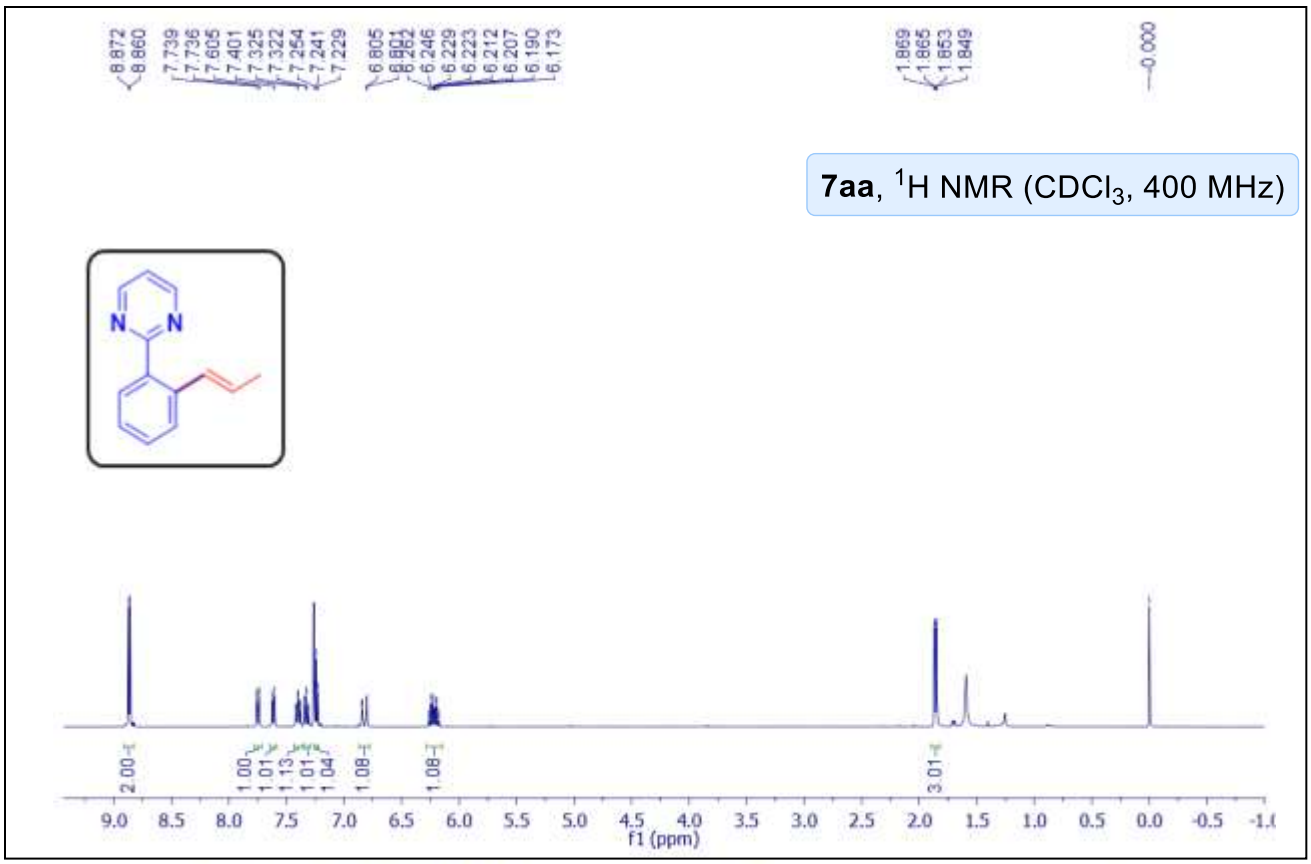
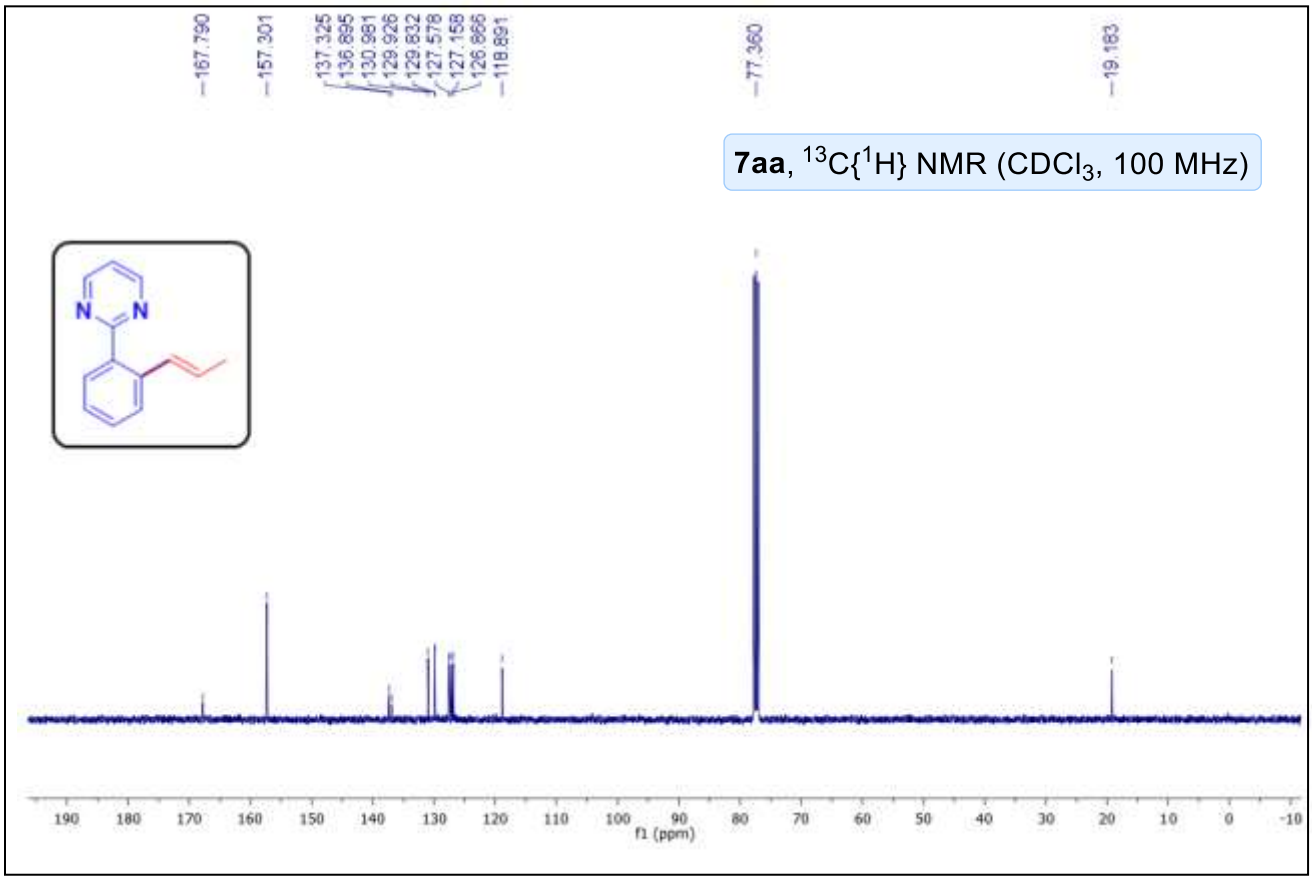


7aa, ^{1}H NMR ($CDCl_3$, 400 MHz)



7aa, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)

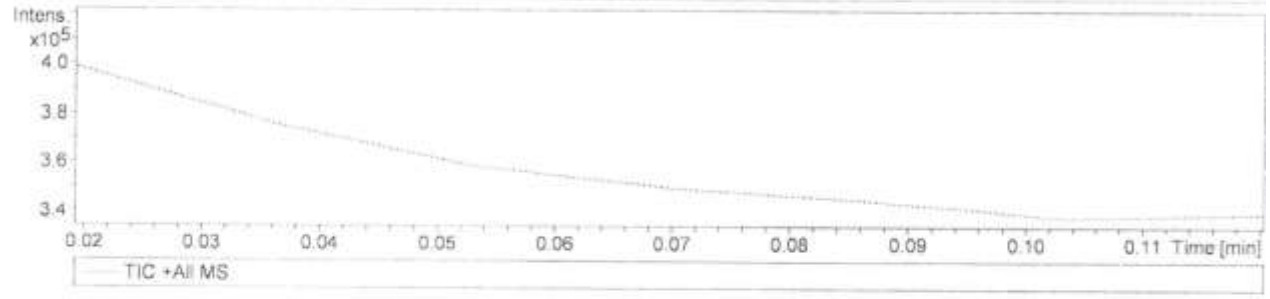
Display Report

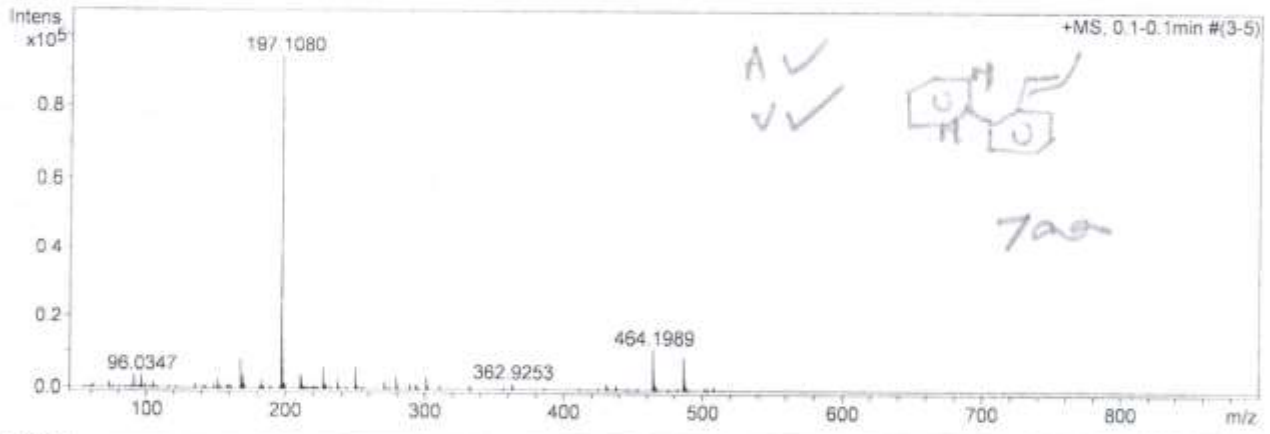
Analysis Info

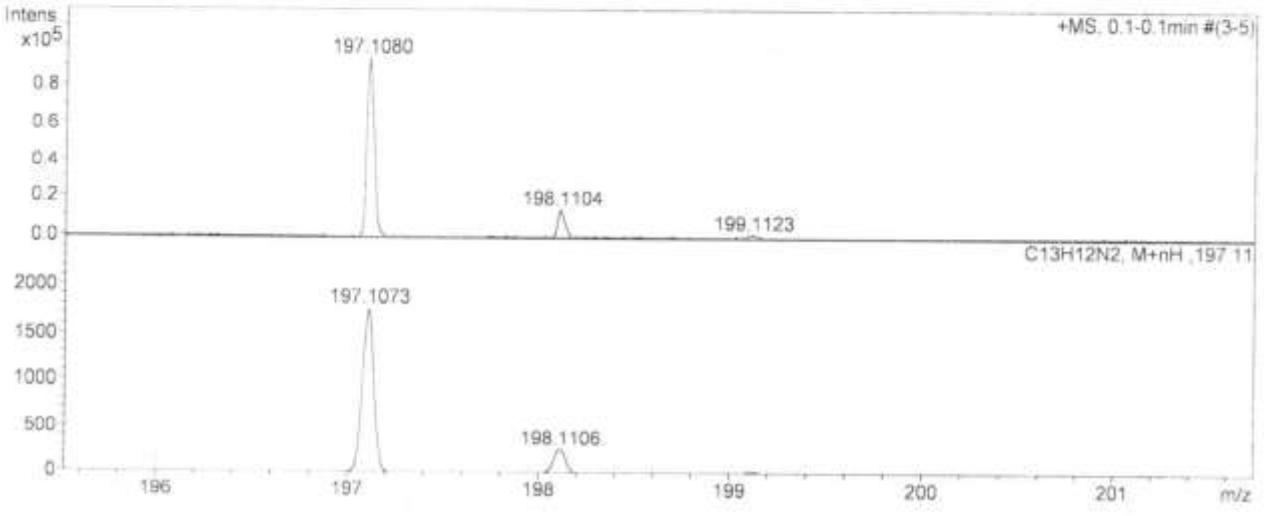
Analysis Name	D:\Data\MAR-2021\PCR\24032021_PCR_PB_1817.d	Acquisition Date	3/24/2021 3:14:09 PM
Method	Pos_tune_low.m	Operator	Amit S.Sahu
Sample Name	Tmix-131118	Instrument	micrOTOF-Q II 10337
Comment			

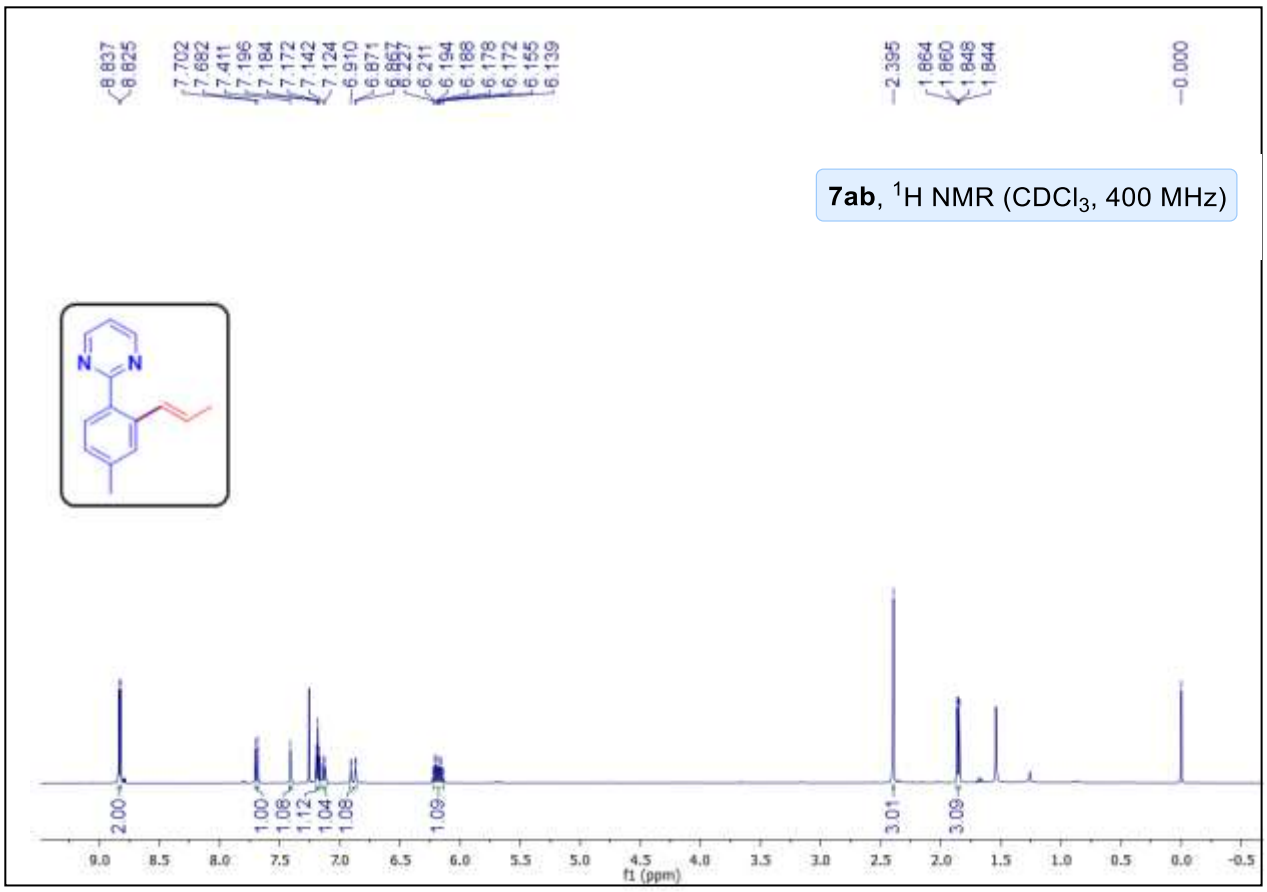
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

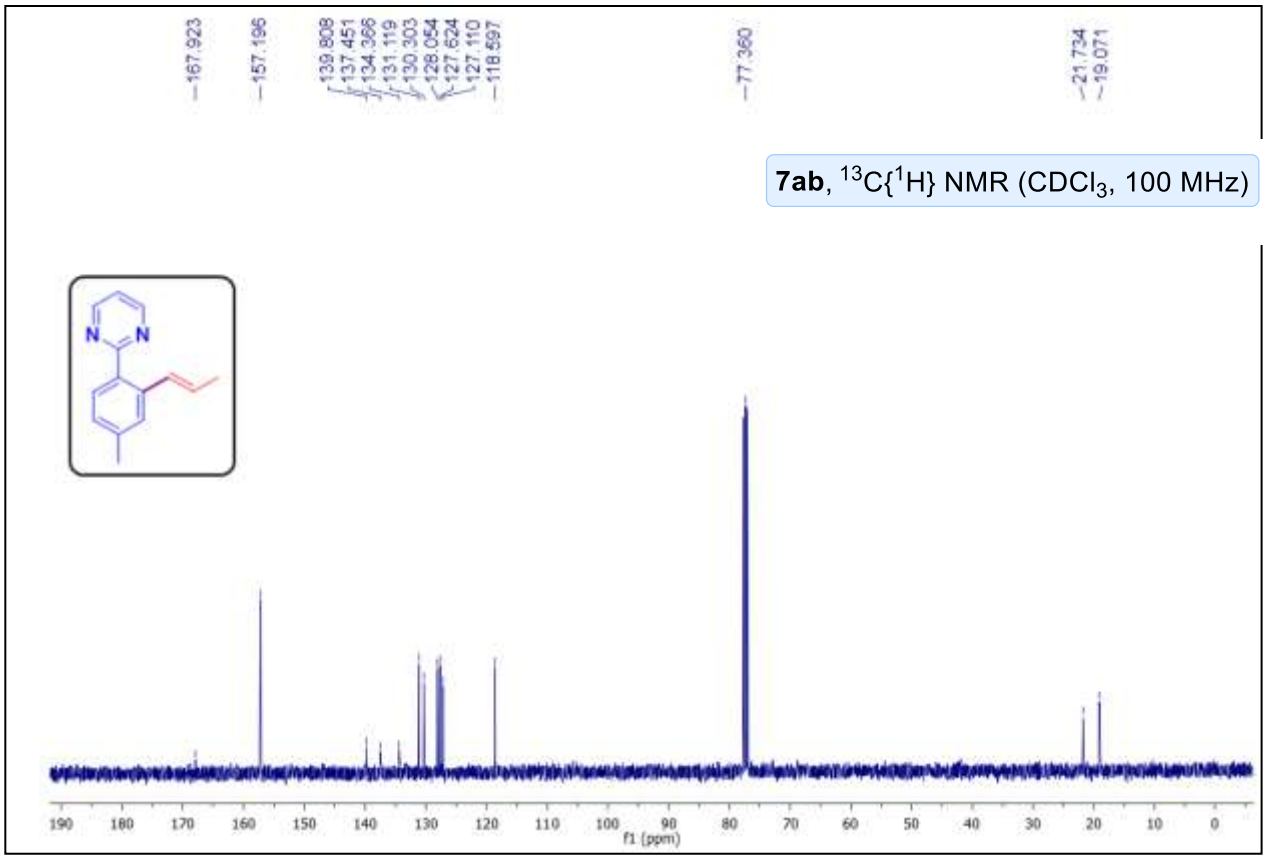








7ab, ^{1}H NMR ($CDCl_3$, 400 MHz)



7ab, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)

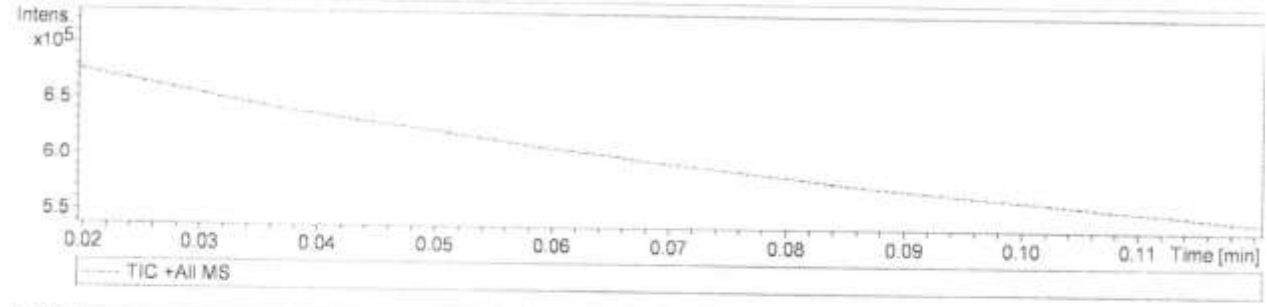
Display Report

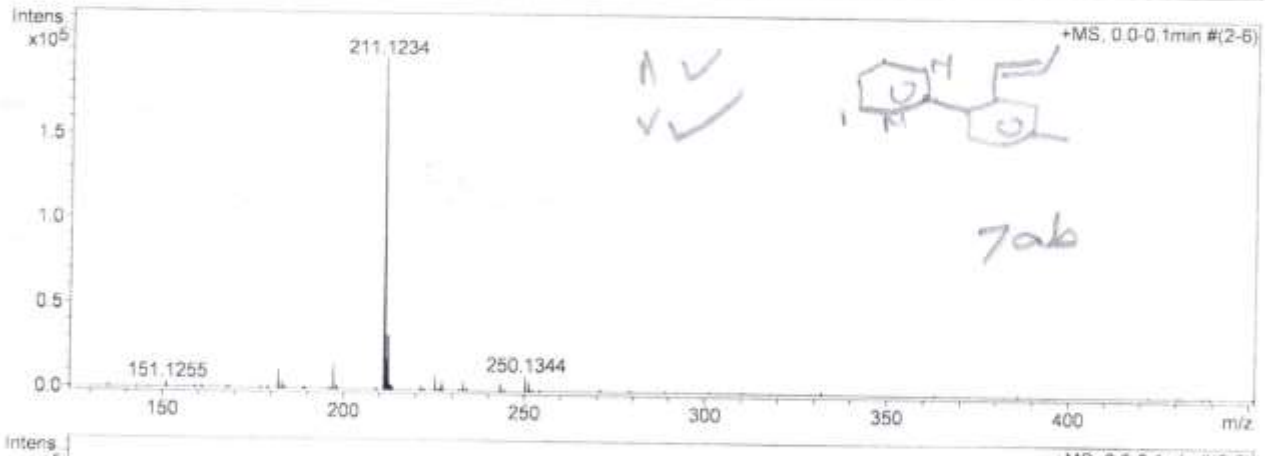
Analysis Info

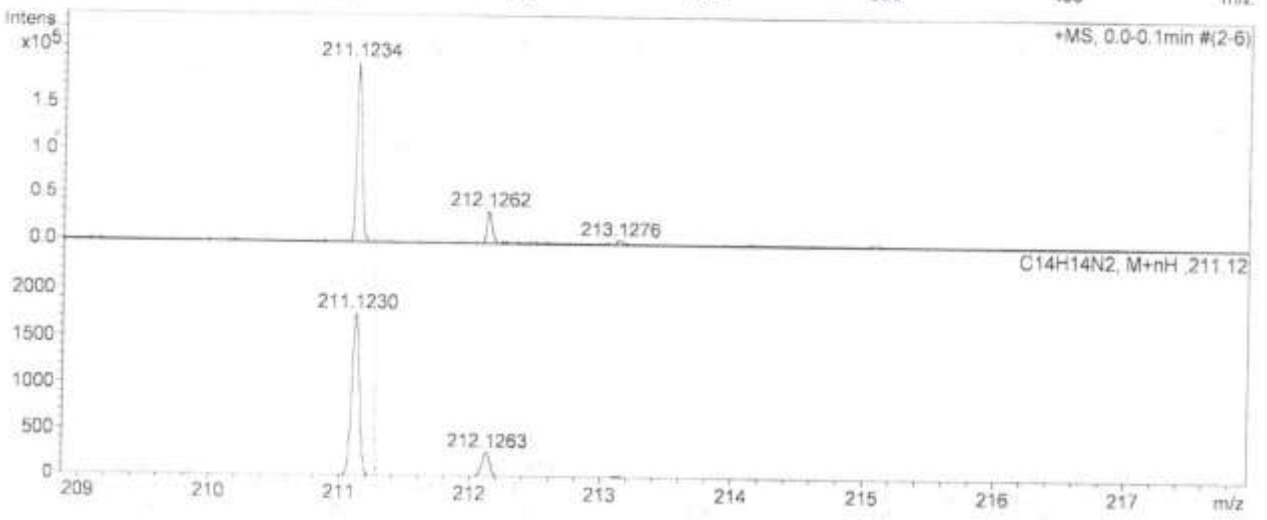
Analysis Name	D:\Data\MAR-2021\PCR\24032021_PCR_PB_1826.d	Acquisition Date	3/24/2021 3:16:13 PM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	Amit S.Sahu
Comment		Instrument	micrOTOF-Q II 10337

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







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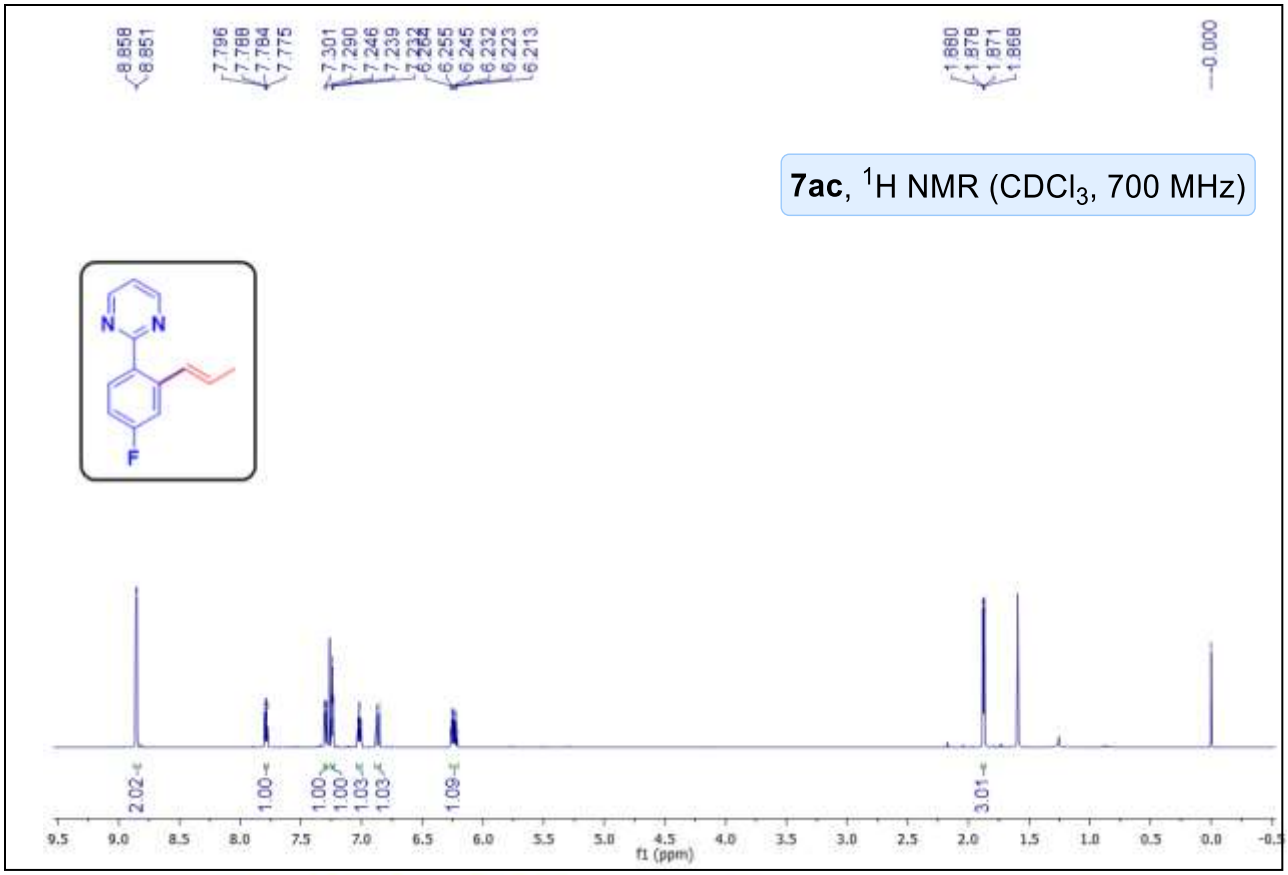
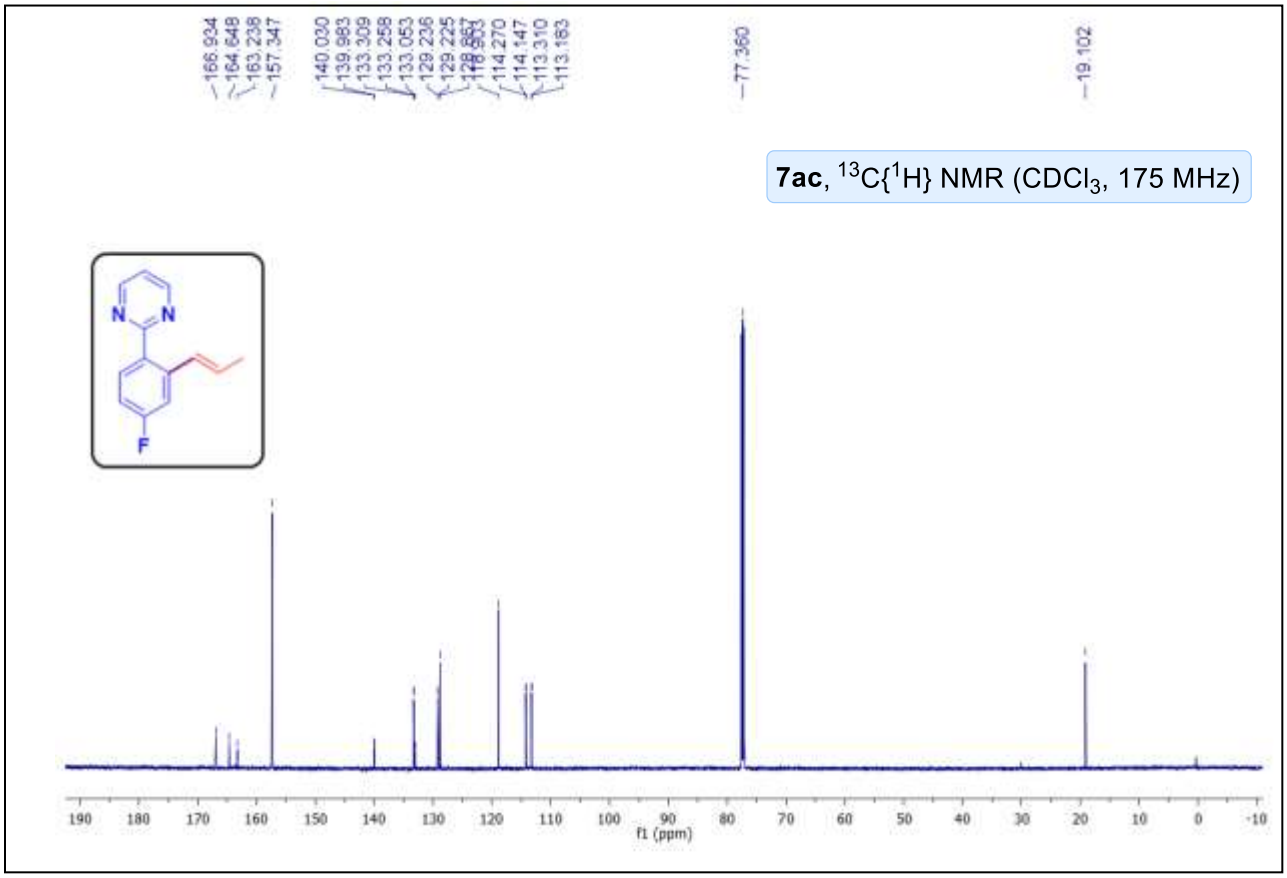
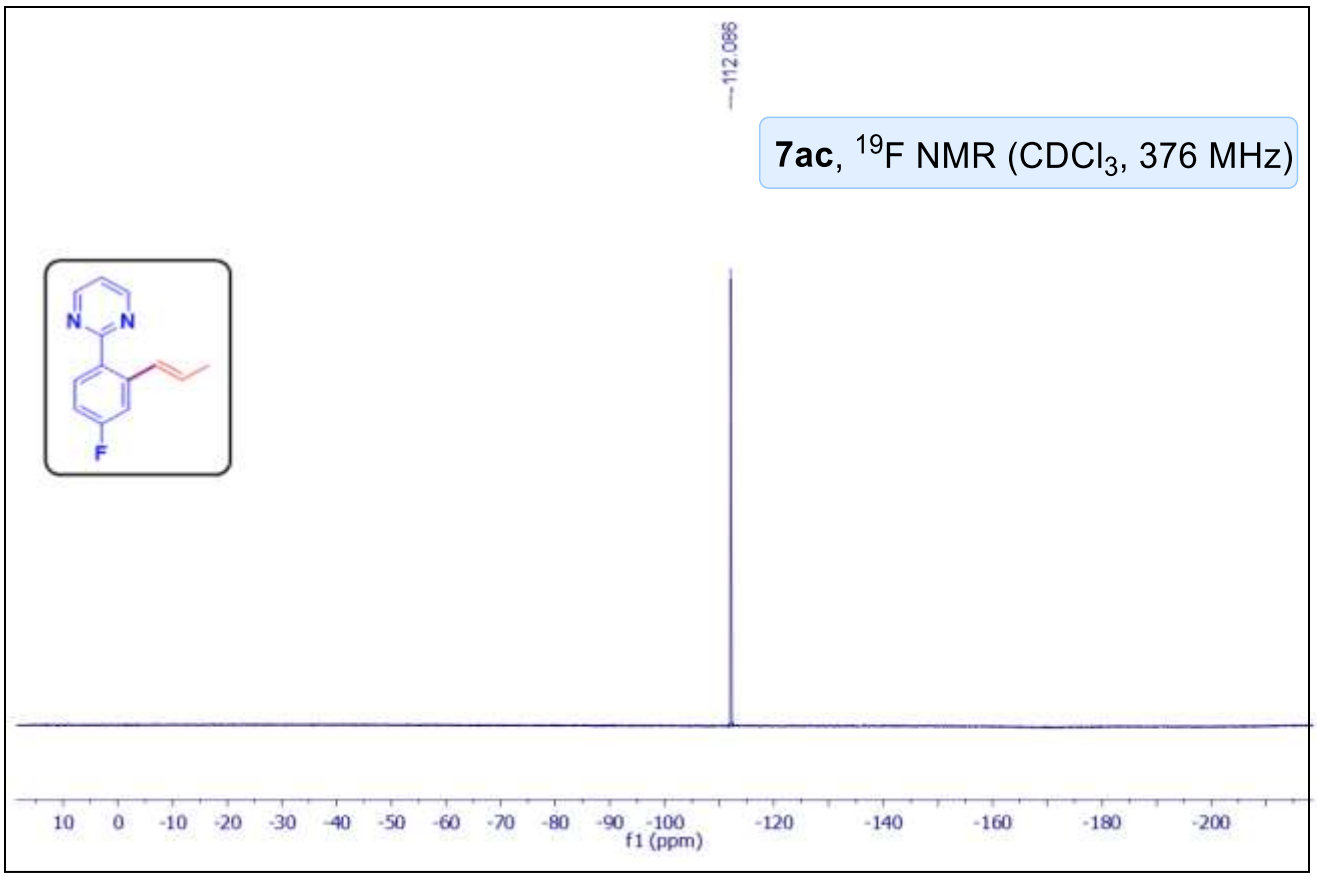


7ac, ^{1}H NMR ($CDCl_3$, 700 MHz)



7ac, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 175 MHz)


-112.086
7ac, 19F NMR (CDCl3, 376 MHz)
N
N
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)

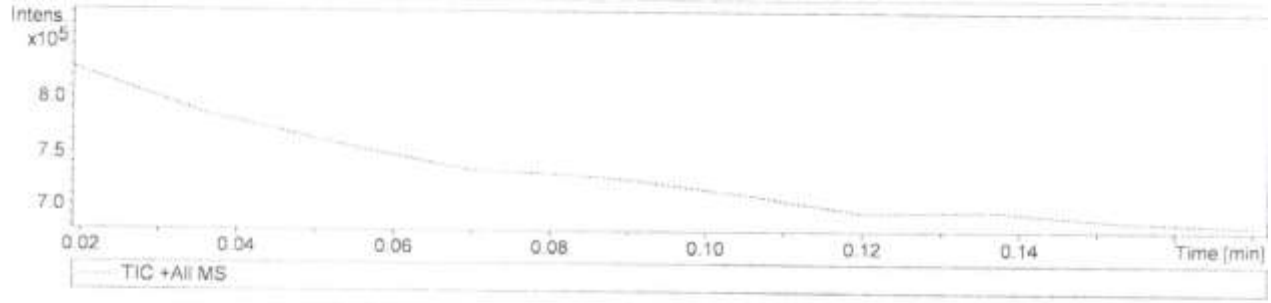
Display Report

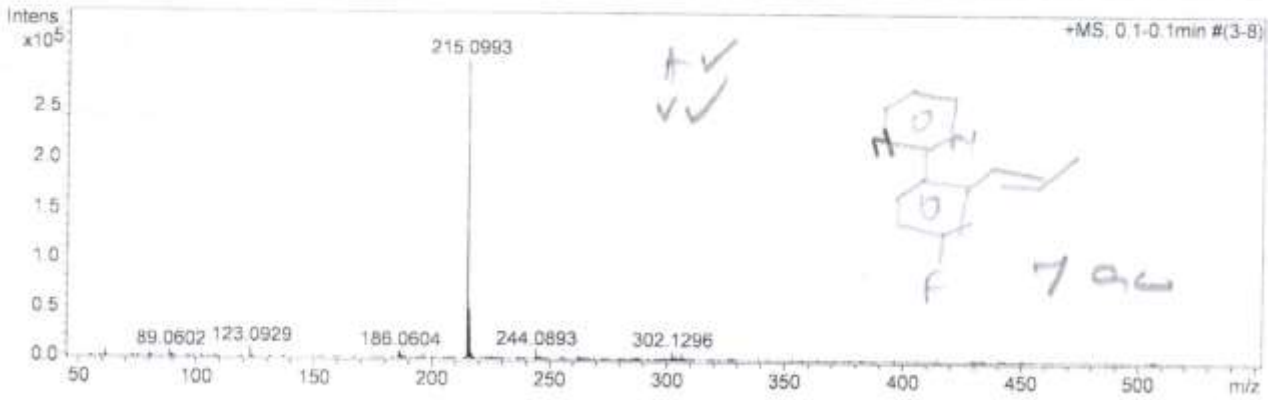
Analysis Info

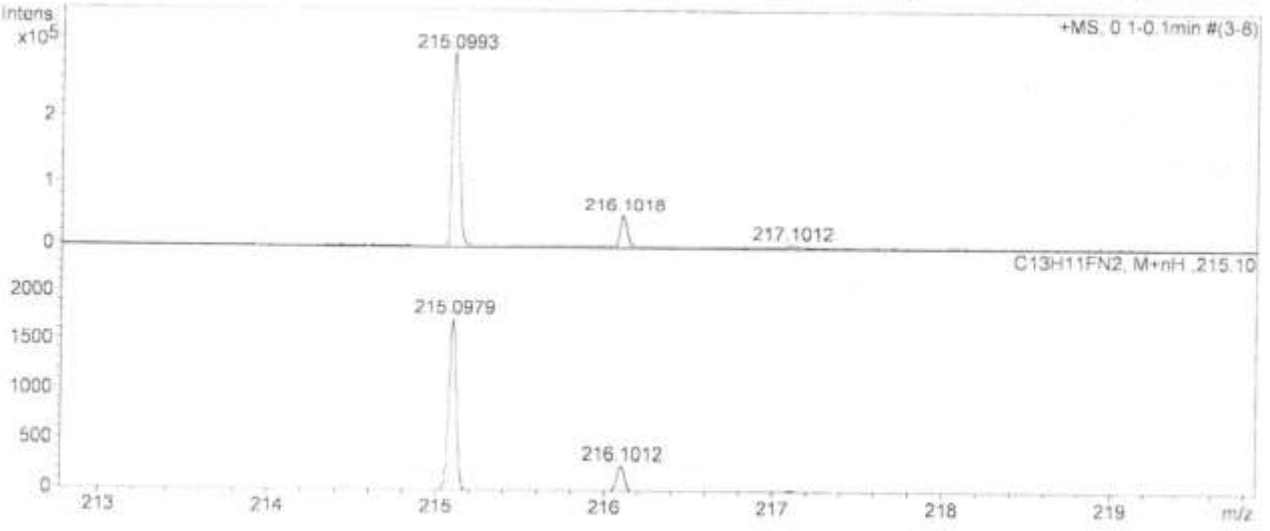
Analysis Name	D:\Data\MAR-2021\PCR\16032021_PCR_PB_1837 d	Acquisition Date	3/16/2021 3:25:47 PM
Method	Pos_tune_low.m	Operator	Amit S Sahu
Sample Name	Tmix-131118	Instrument	micrOTOF-Q II 10337
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







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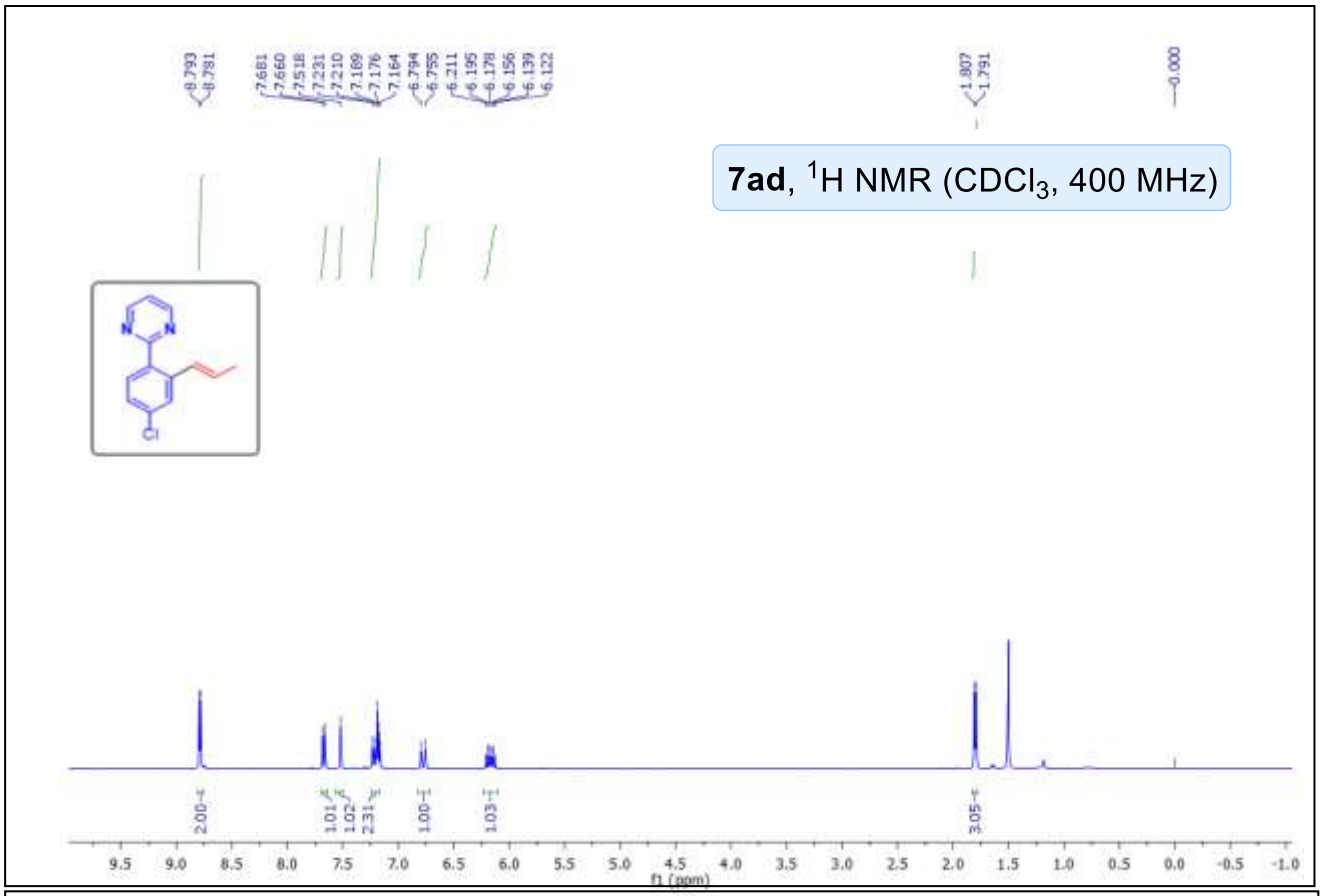
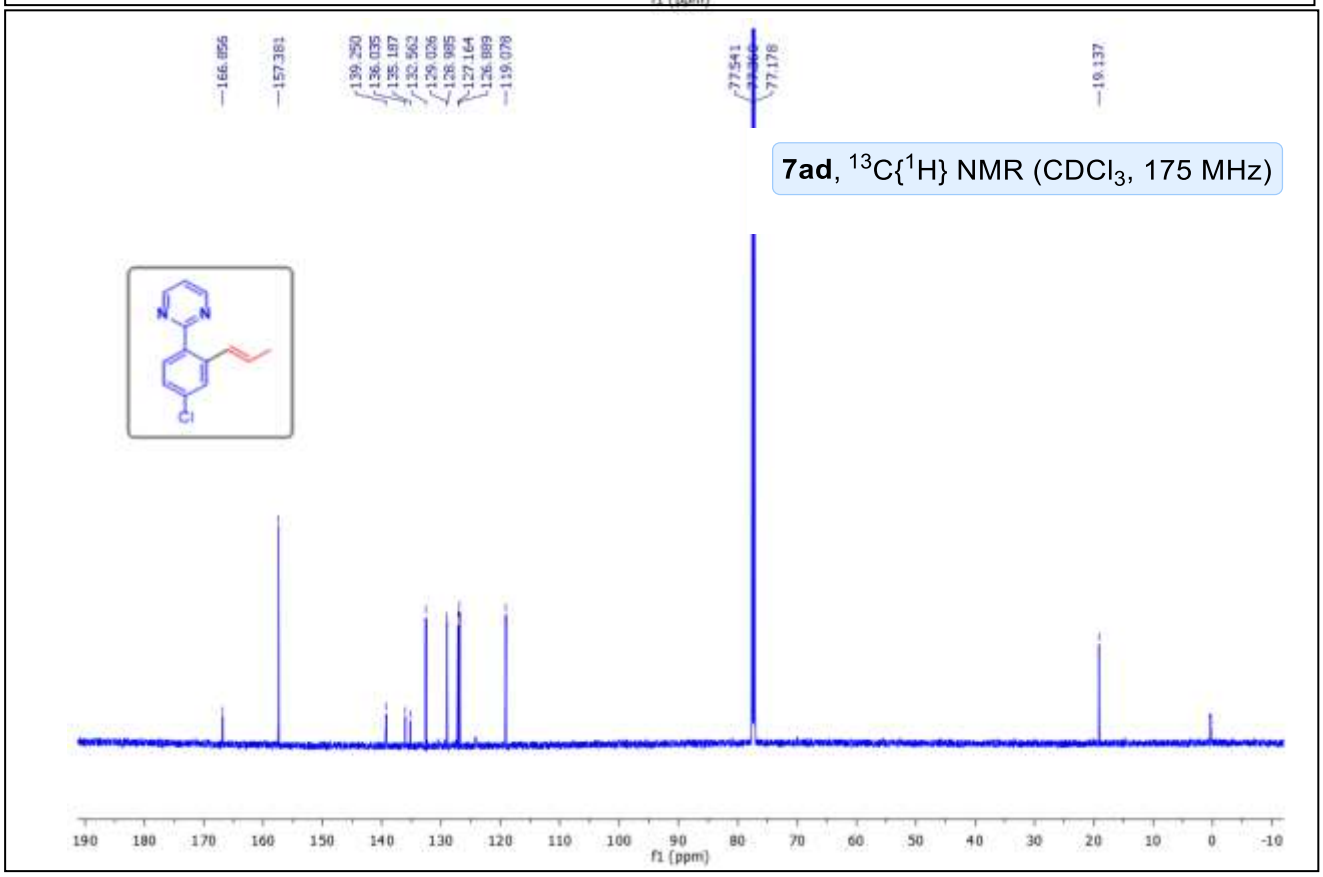


7ad, ^{1}H NMR ($CDCl_3$, 400 MHz)



7ad, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 175 MHz)

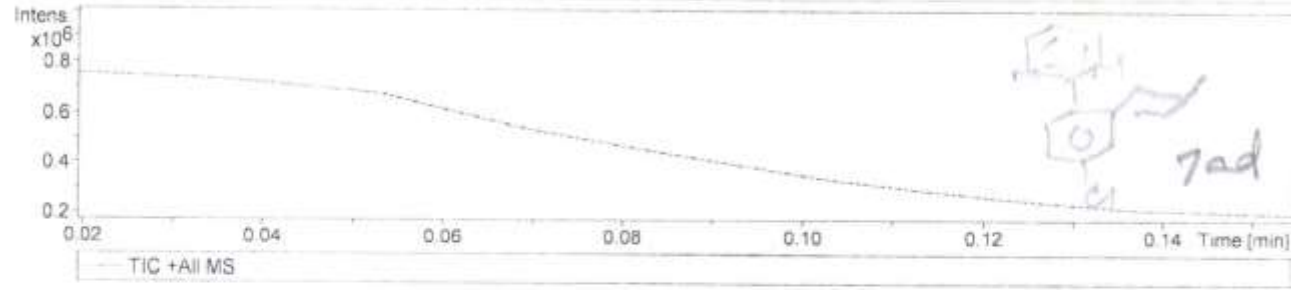
Display Report

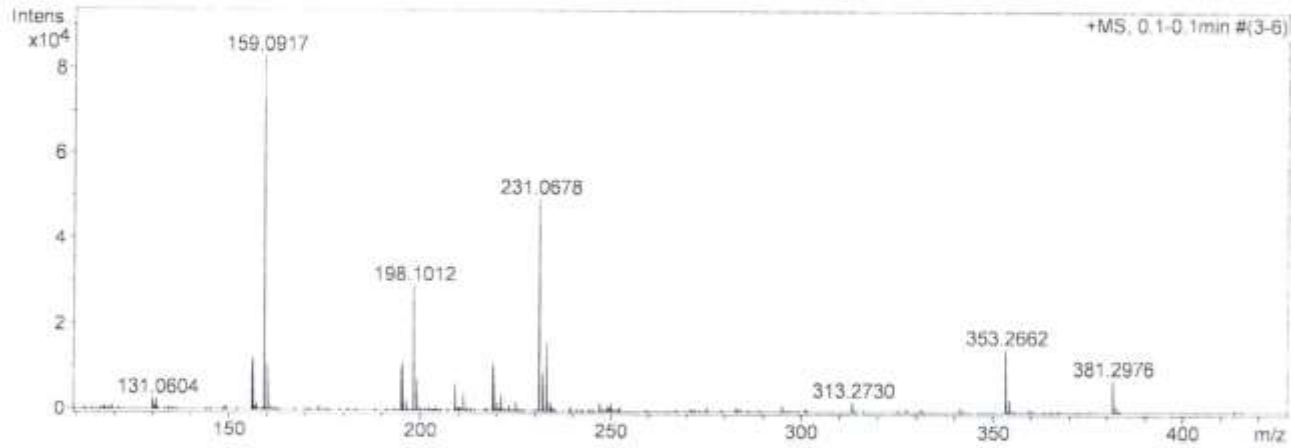
Analysis Info

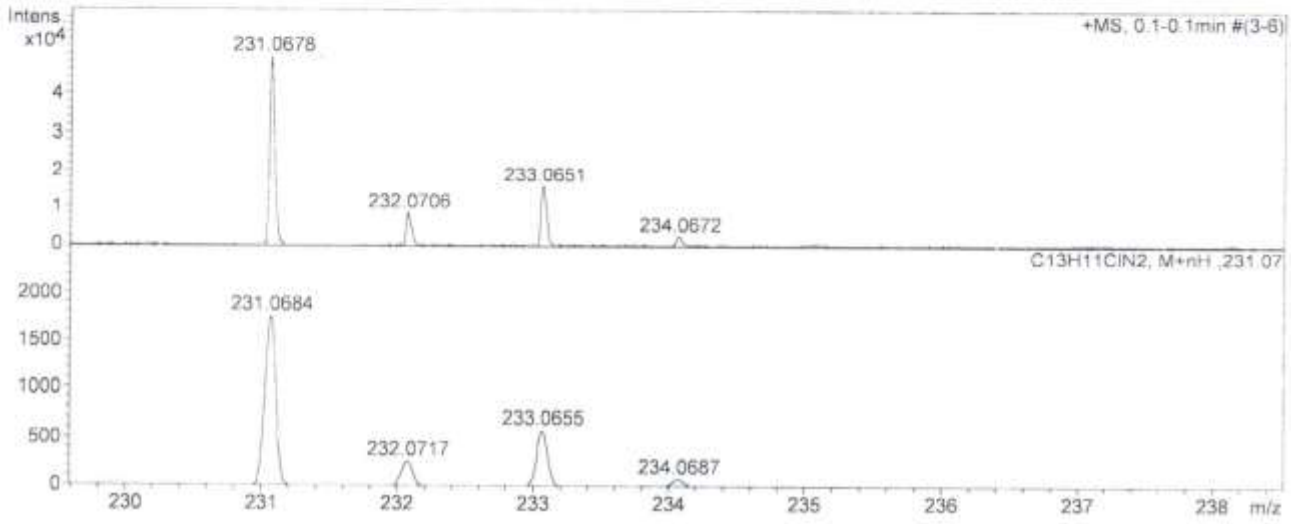
Analysis Name	D:\Data\FEB-2021\PCR\18022021_PCR_TN_1476.d	Acquisition Date	2/22/2021 11:07:49 AM
Method	Pos_tune_low.m	Operator	Amit S.Sahu
Sample Name	Tmix-131118	Instrument	micrOTOF-Q II 10337
Comment			

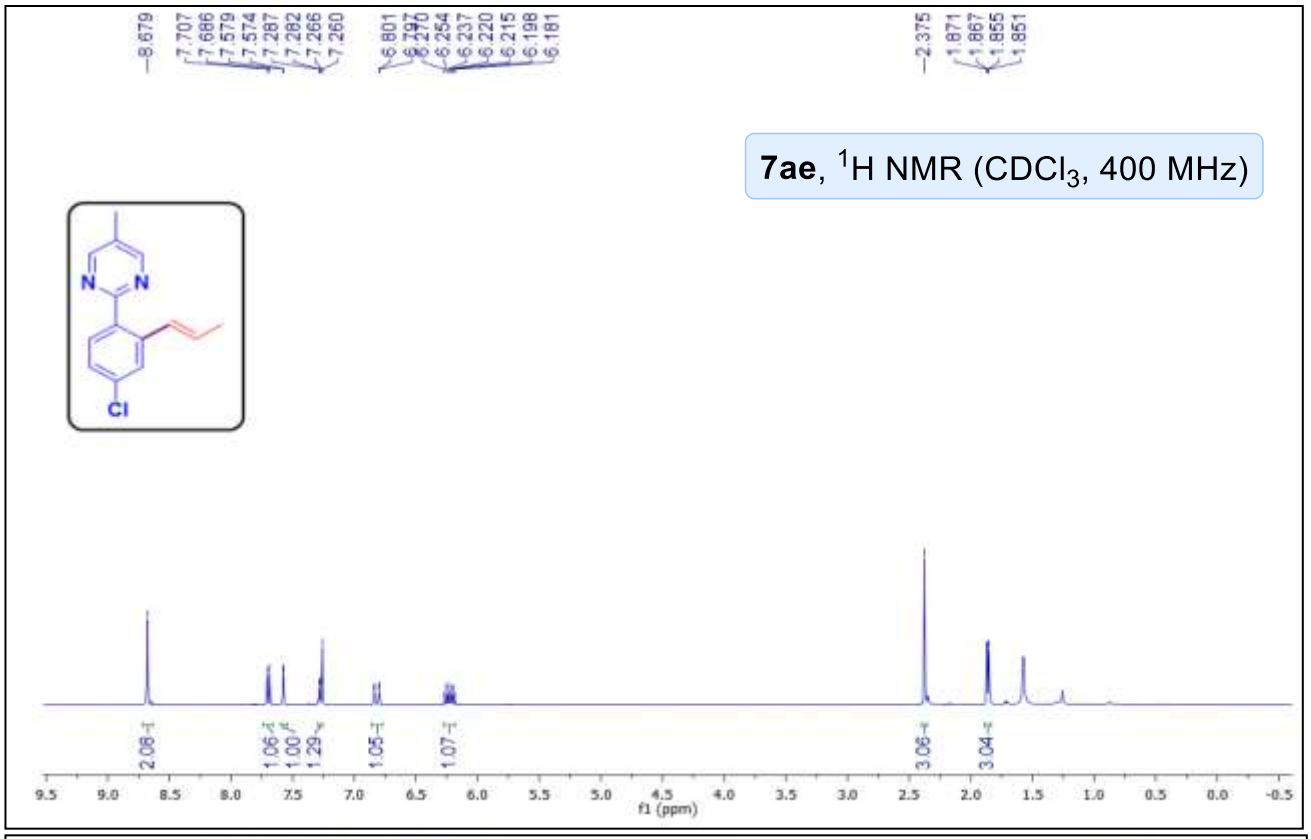
Acquisition Parameter

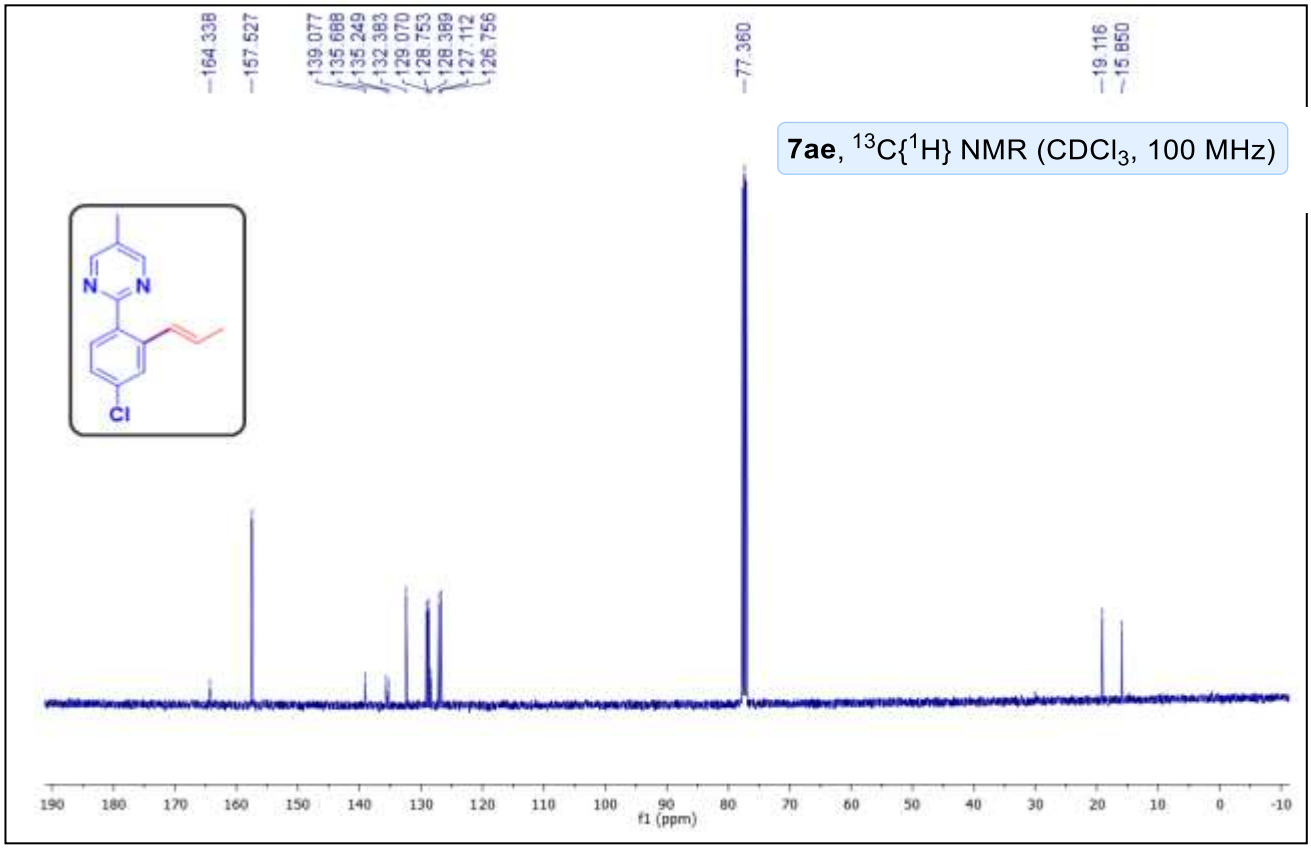
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste








8.679
7.707
7.686
7.579
7.574
7.287
7.282
7.266
7.260
6.801
6.797
6.276
6.254
6.237
6.220
6.215
6.198
6.181
2.375
1.871
1.867
1.855
1.851
7ae, 1H NMR (CDCl3, 400 MHz)
N
N
Cl
2.06
1.06
1.00
1.29
1.05
1.07
3.06
3.04
f1 (ppm)


164.338
157.527
139.077
135.688
135.249
132.383
129.070
128.753
128.389
127.112
126.756
77.360
19.116
15.850
7ae, 13C{1H} NMR (CDCl3, 100 MHz)
N
N
Cl
f1 (ppm)

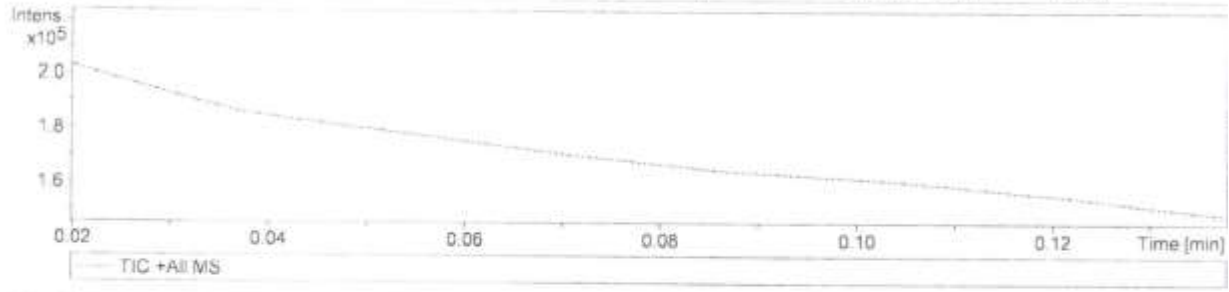
Display Report

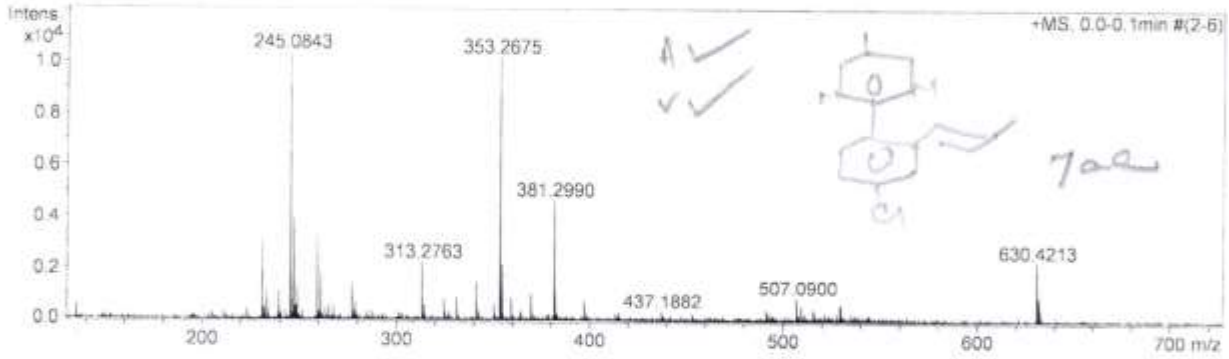
Analysis Info

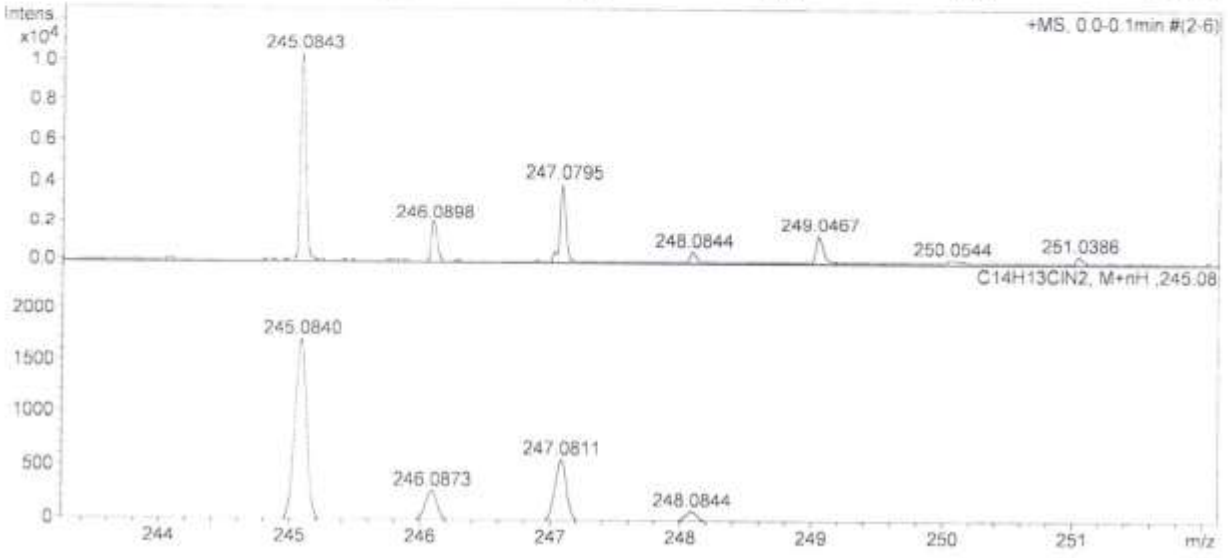
Analysis Name	D:\Data\APR-2021\HSB\26042021_HSB_R_1771.d	Acquisition Date	4/26/2021 3:42:06 PM
Method	Pos_tune_low.m	Operator	Amit S.Sahu
Sample Name	Tmix-131118	Instrument	micrOTOF-Q II 10337
Comment			

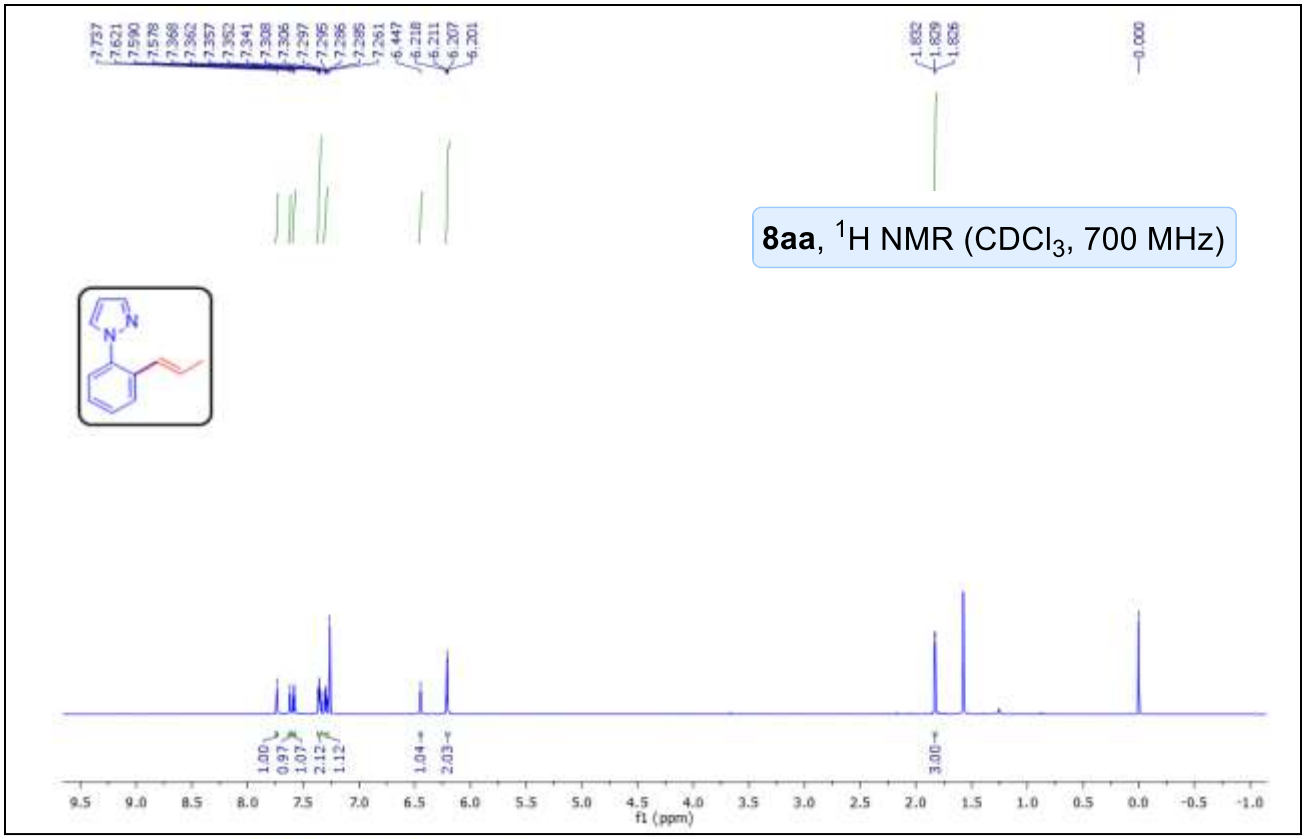
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

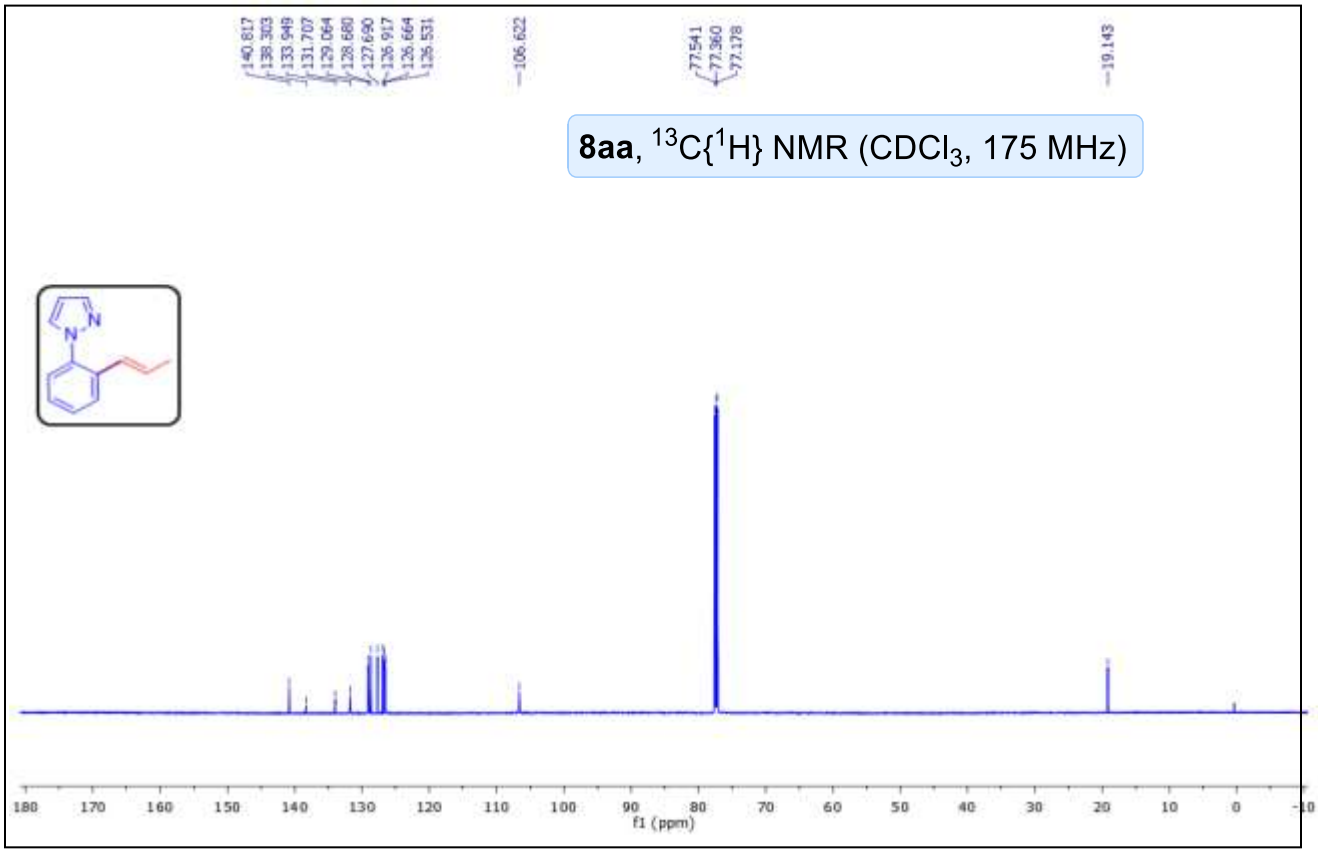




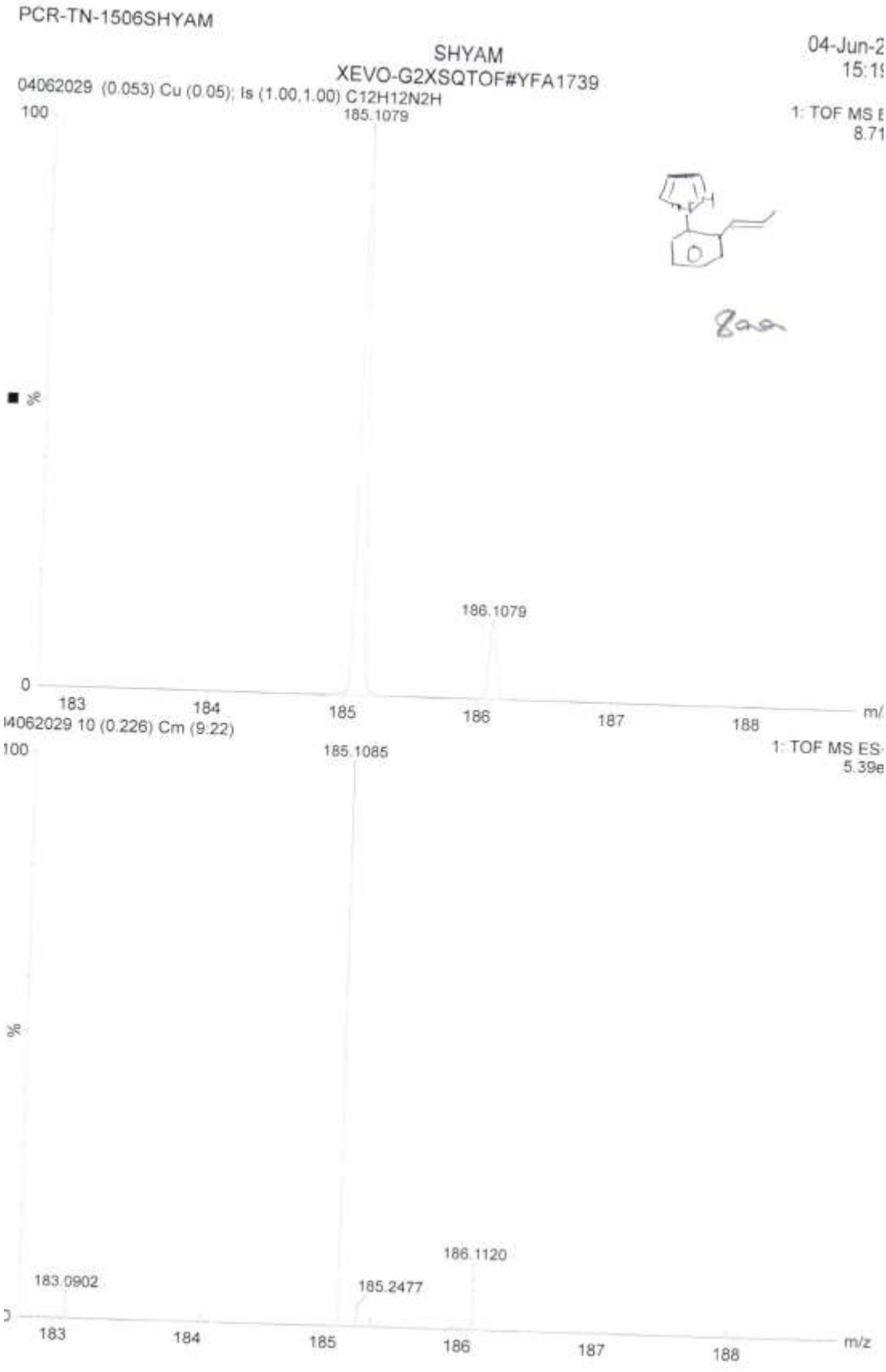


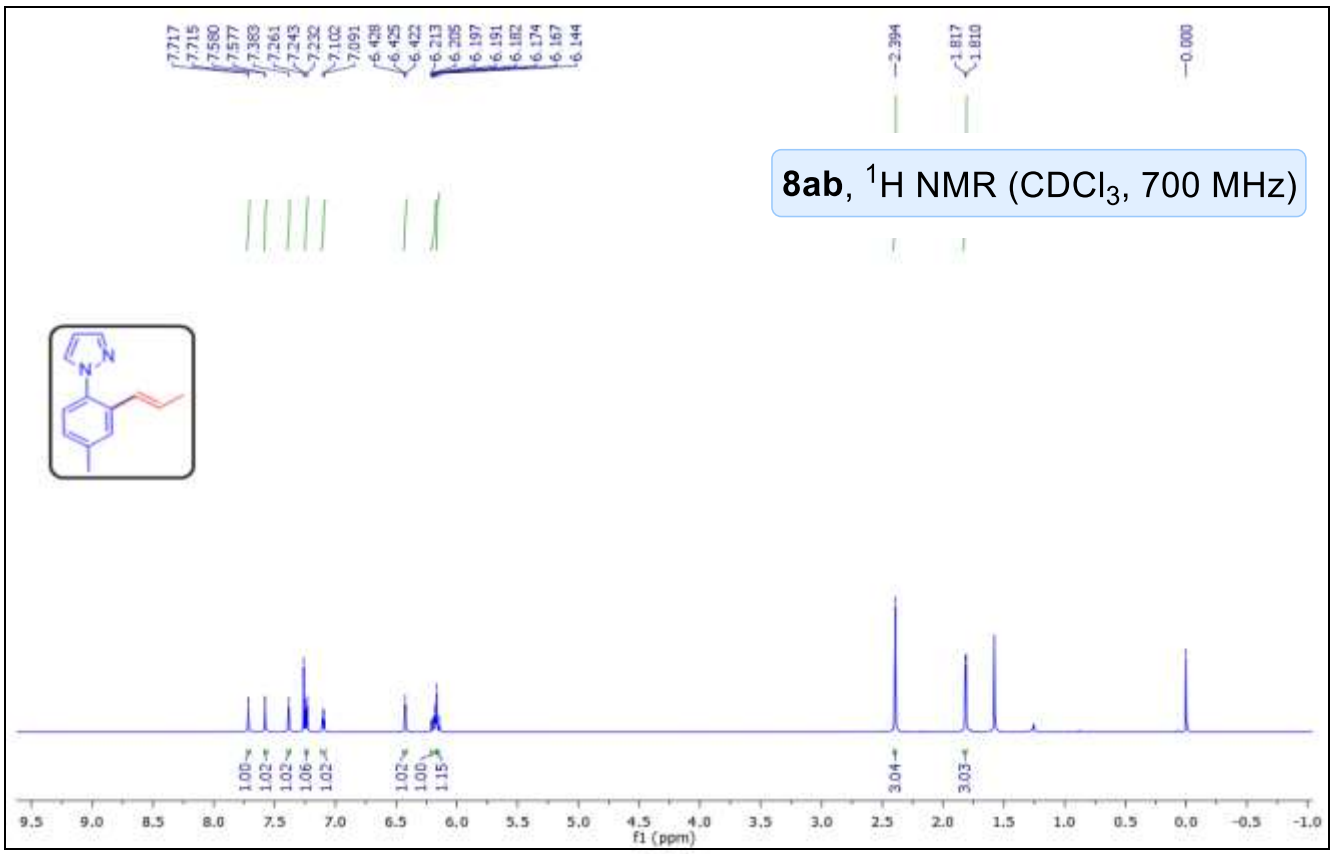


8aa, ^{1}H NMR ($CDCl_3$, 700 MHz)

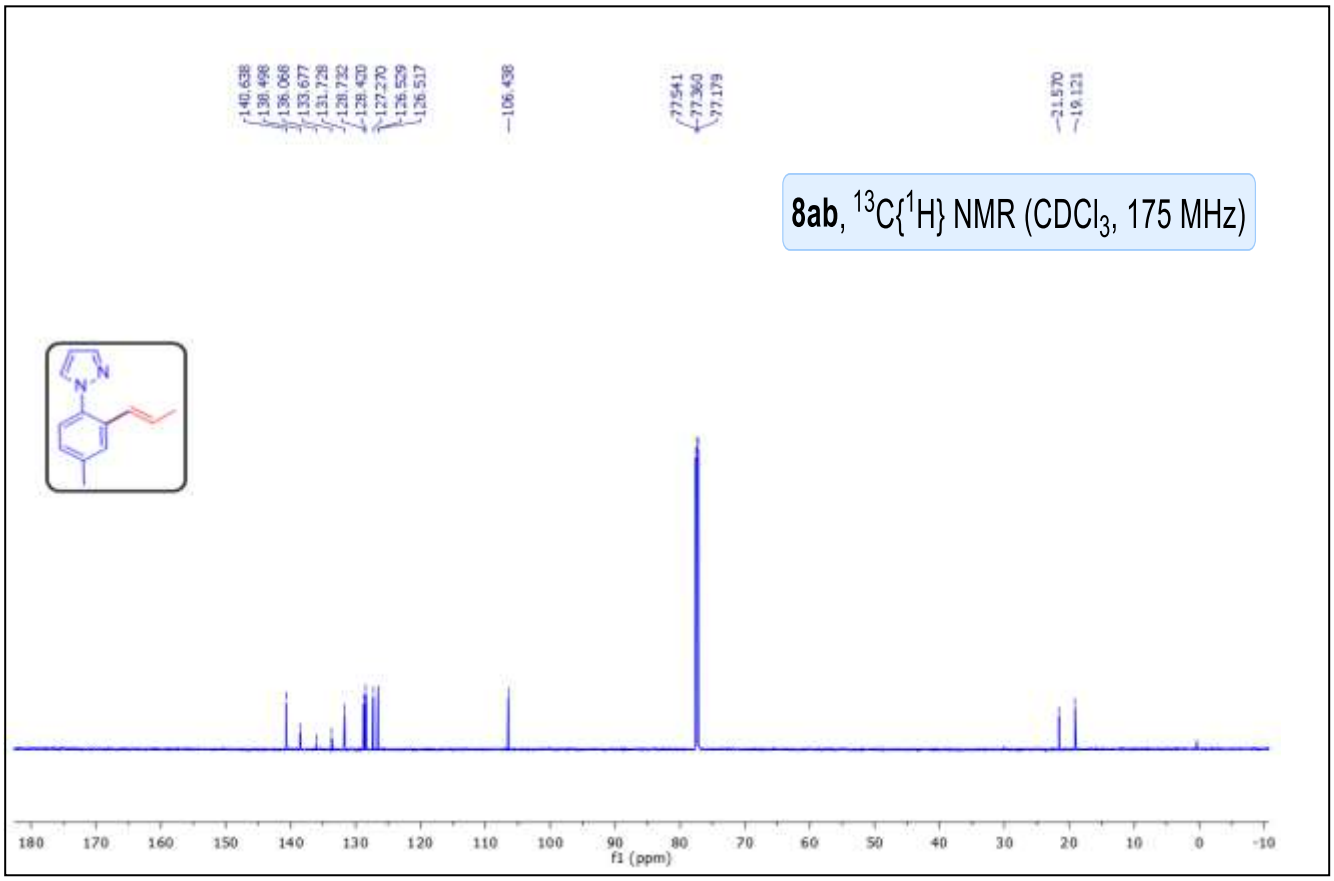


8aa, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 175 MHz)


PCR-TN-1506SHYAM
SHYAM
XEVO-G2XSQTOF#YFA1739
04-Jun-2
15:1
04062029 (0.053) Cu (0.05); Is (1.00,1.00) C12H12N2H
100
185.1079
1: TOF MS E
8.71
8aa
%
186.1079
0
183
184
185
186
187
188
m/
04062029 10 (0.226) Cm (9.22)
100
185.1085
1: TOF MS ES
5.39e
%
186.1120
183.0902
185.2477
0
183
184
185
186
187
188
m/z



8ab, ^{1}H NMR ($CDCl_3$, 700 MHz)



8ab, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 175 MHz)

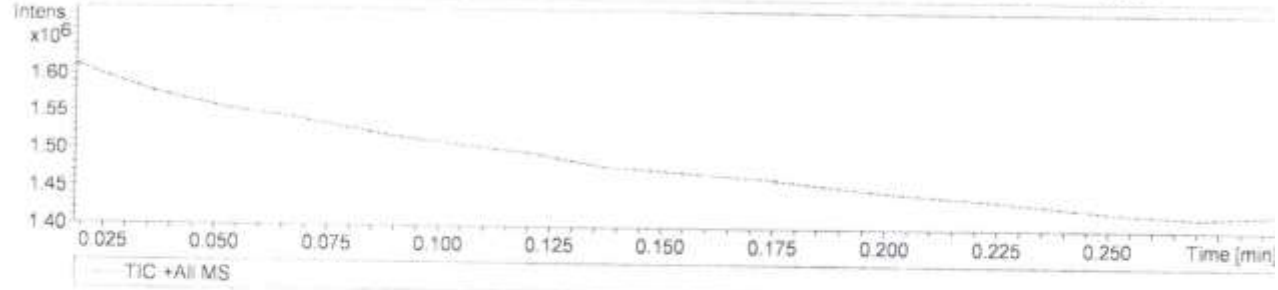
Display Report

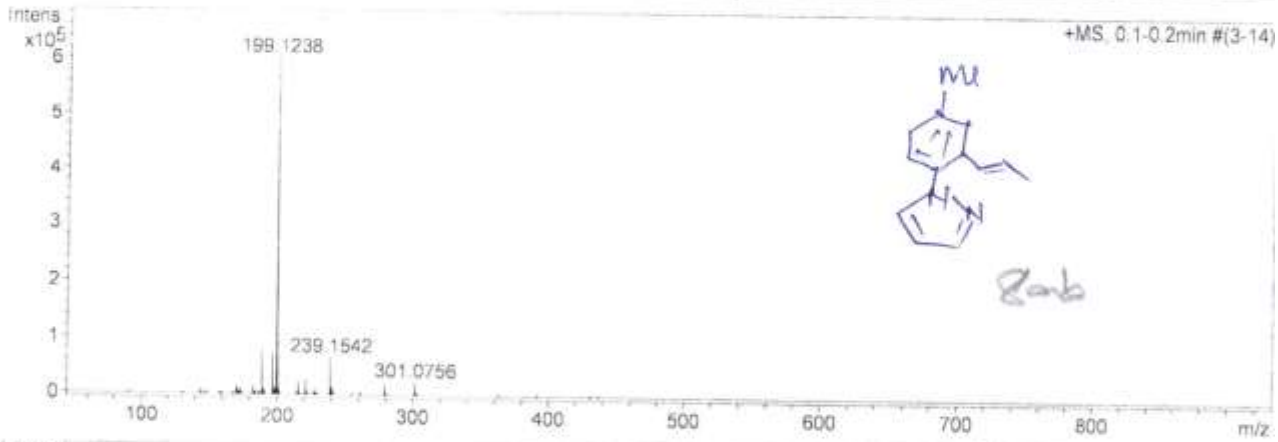
Analysis Info

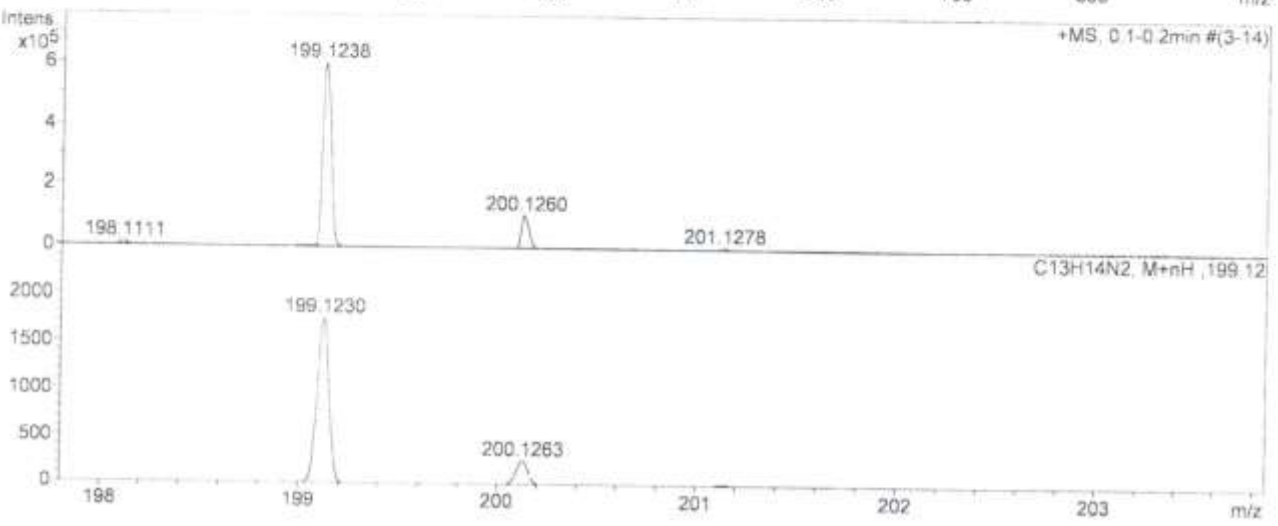
Analysis Name	D:\Data\MAR-2021\PCR\26032021_PCR_TN_1511.d	Acquisition Date	3/26/2021 3:18:32 PM
Method	Pos_tune_low.m	Operator	Amit S.Sahu
Sample Name	Tmix-131118	Instrument	micrOTOF-Q II 10337
Comment			

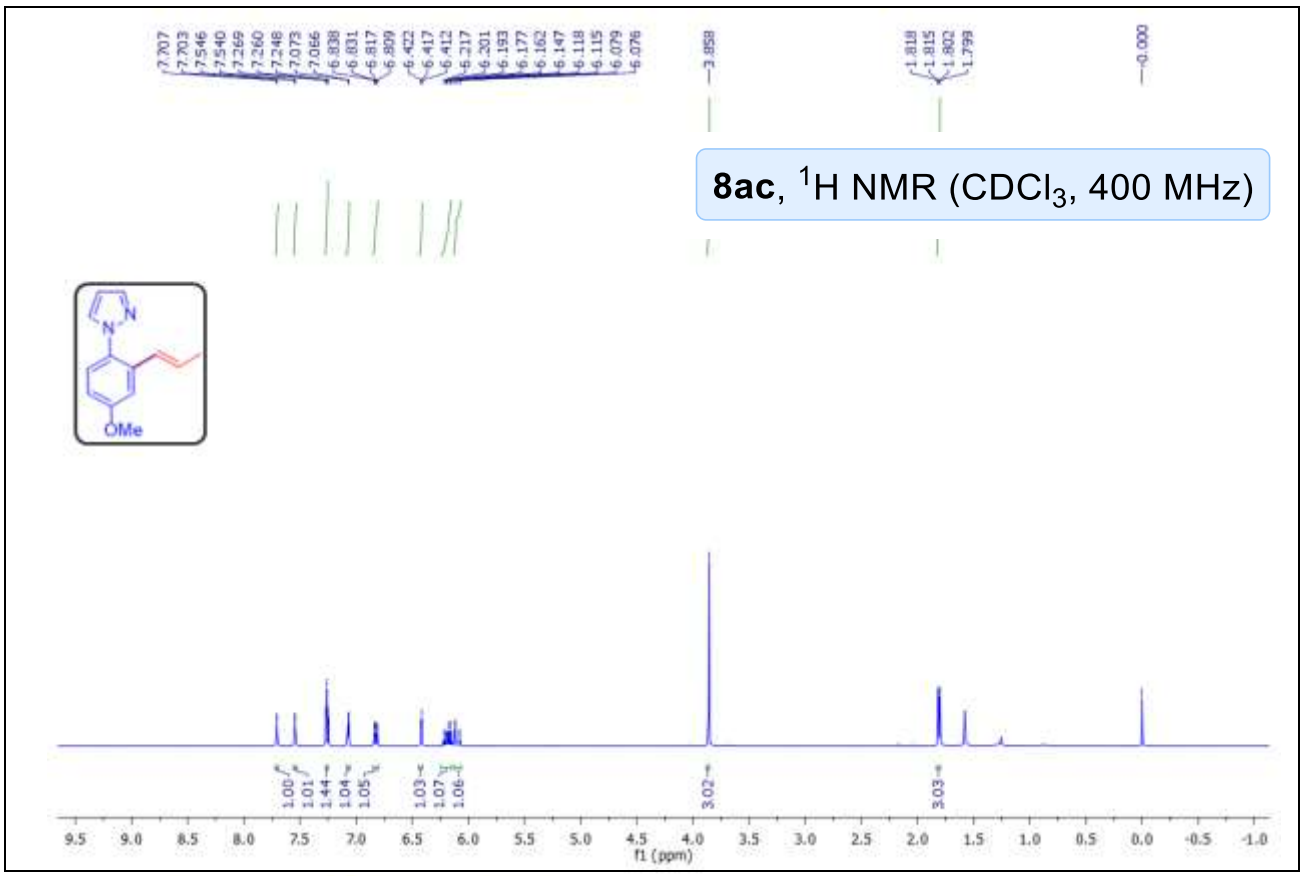
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

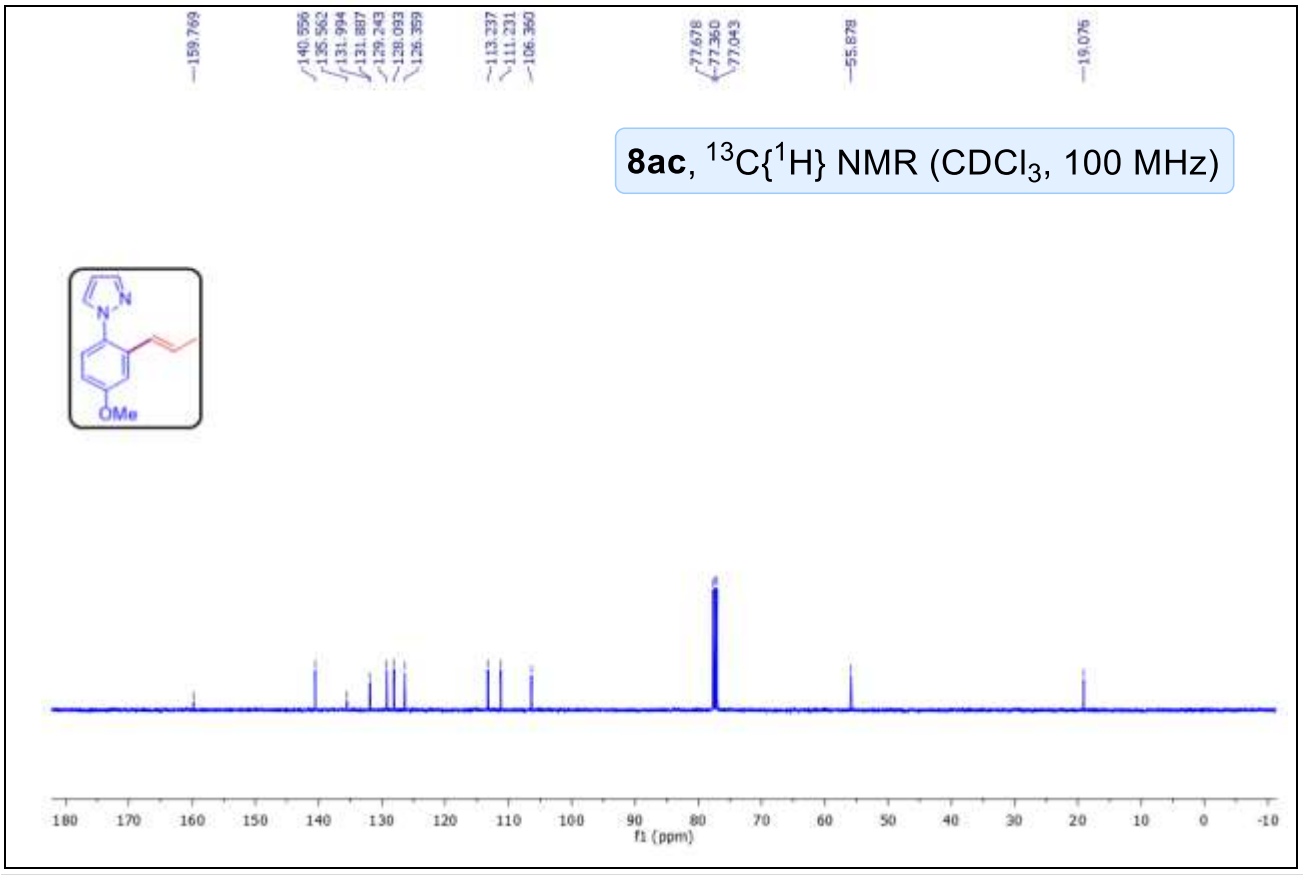








8ac, ^{1}H NMR ($CDCl_3$, 400 MHz)



8ac, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)

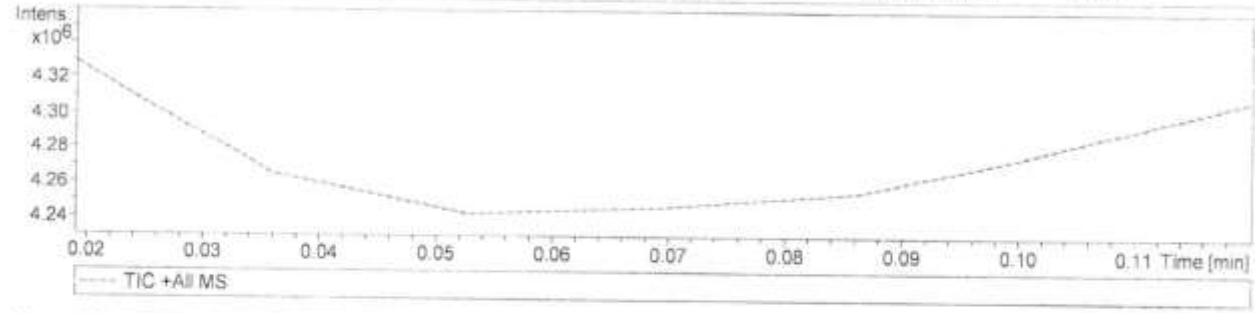
Display Report

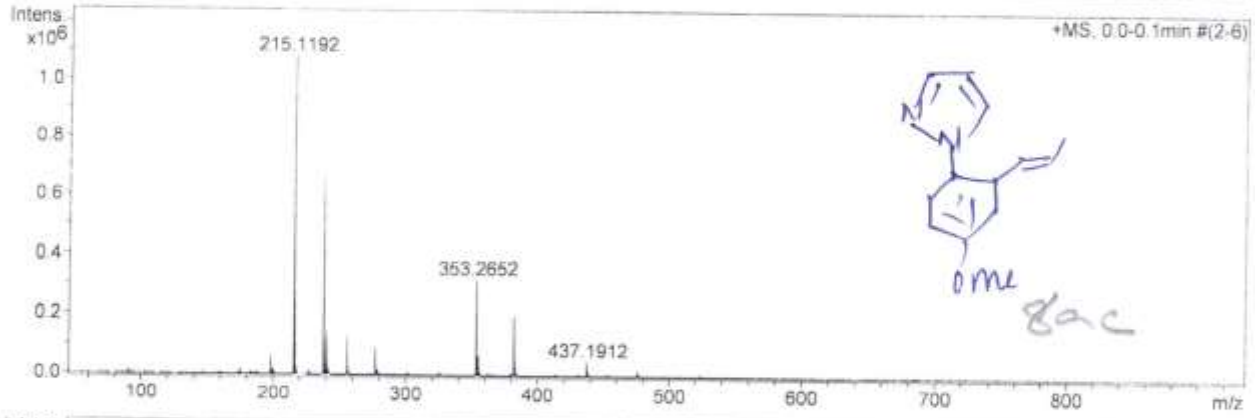
Analysis Info

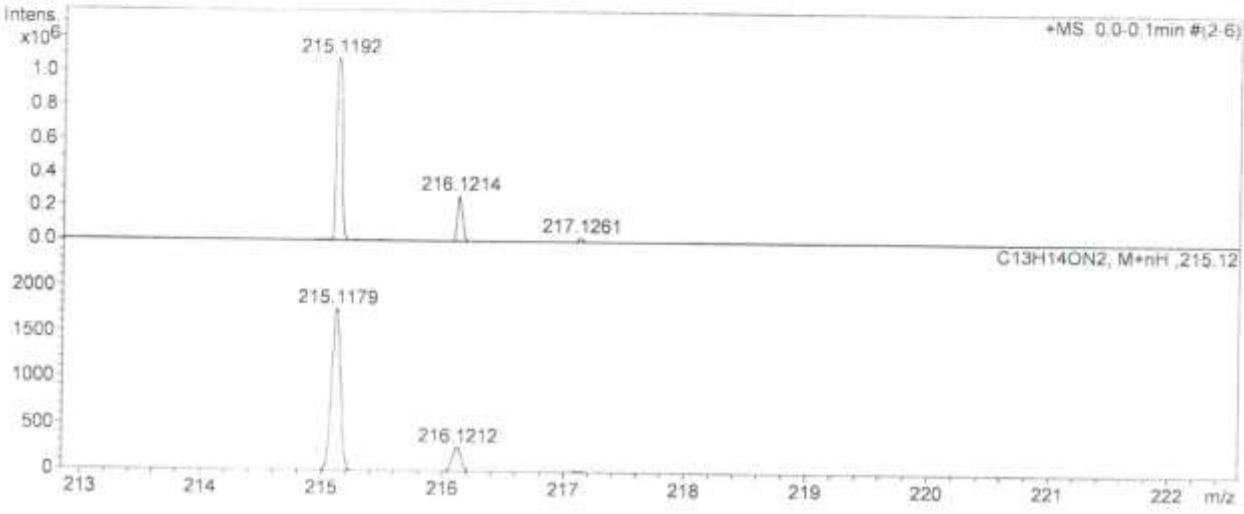
Analysis Name	D:\Data\FEB-2021\PCR\26022021_PCR_TN_1493.d	Acquisition Date	2/26/2021 11:35:33 AM
Method	Pos_tune_low.m	Operator	Amit S.Sahu
Sample Name	Tmix-131118	Instrument	micrOTOF-Q II 10337
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







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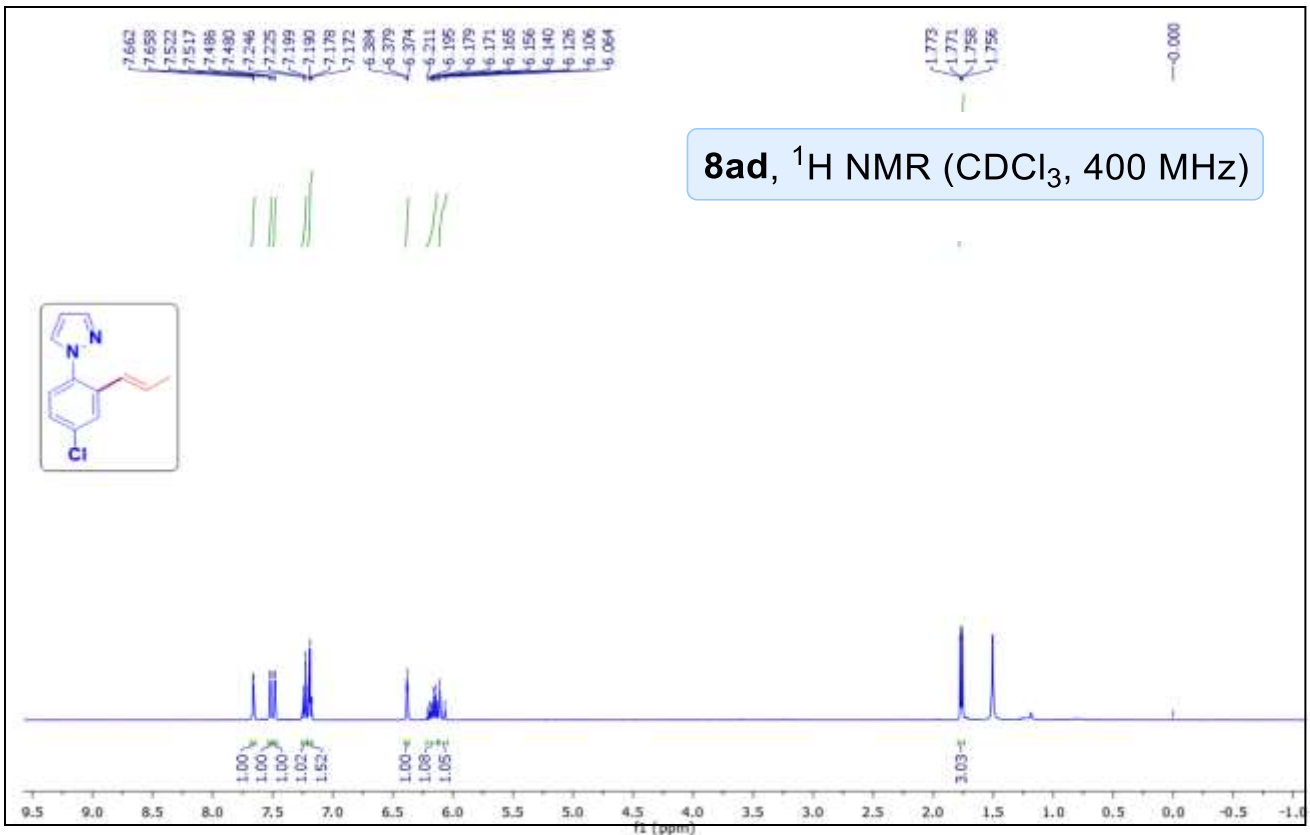
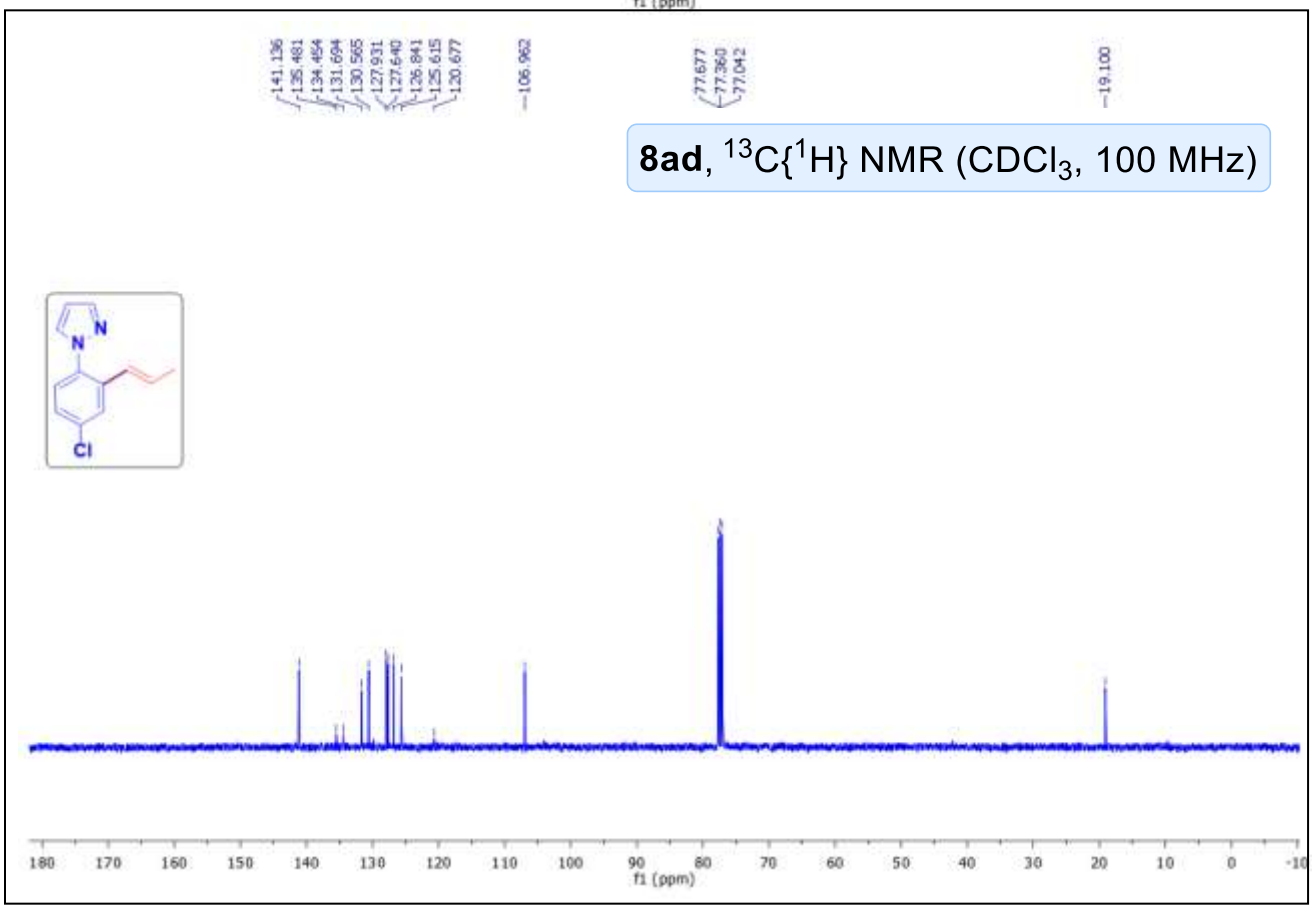

7.662
7.658
7.522
7.517
7.486
7.480
7.246
7.225
7.199
7.190
7.178
7.172
6.384
6.379
6.374
6.211
6.195
6.179
6.171
6.165
6.156
6.140
6.126
6.106
6.064
1.773
1.771
1.758
1.756
0.000
8ad, 1H NMR (CDCl3, 400 MHz)
N
N
Cl
1.00
1.00
1.00
1.02
1.52
1.00
1.08
1.05
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


141.136
135.481
134.454
131.694
130.565
127.931
127.640
126.841
125.615
120.677
106.962
77.677
77.360
77.042
19.100
8ad, 13C{1H} NMR (CDCl3, 100 MHz)
N
N
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

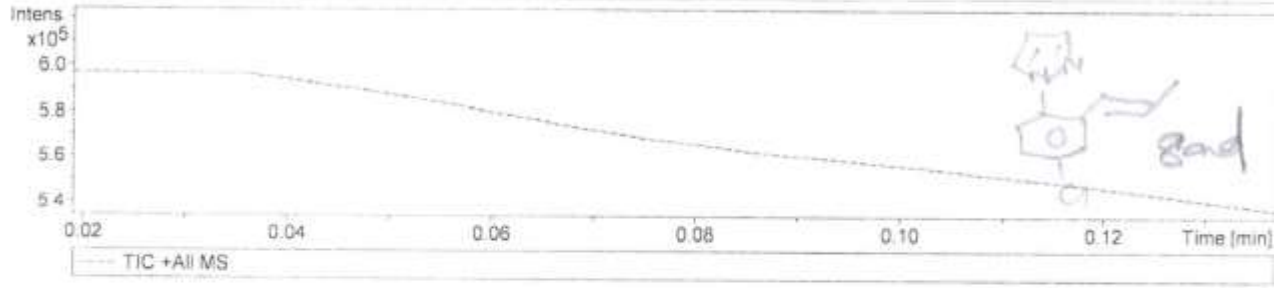
Display Report

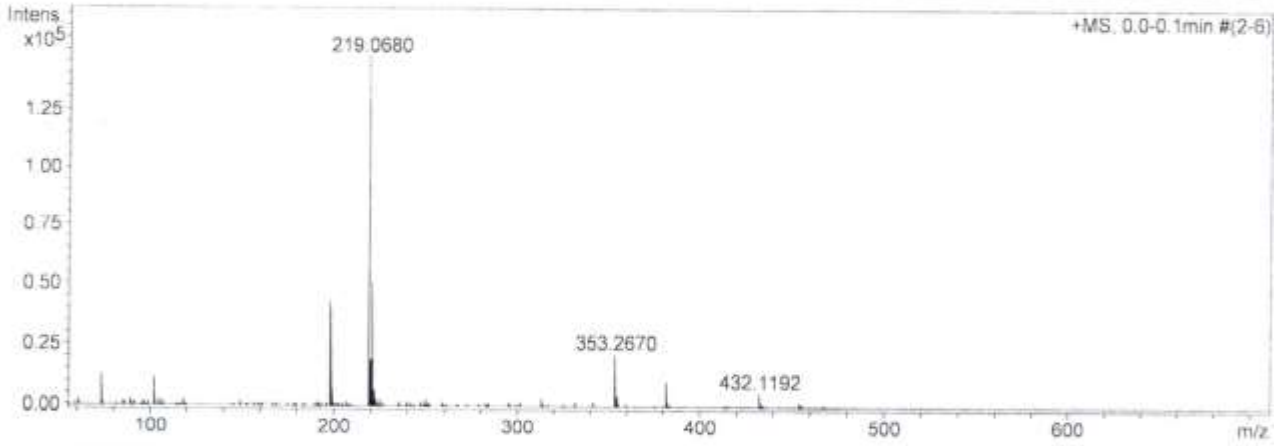
Analysis Info

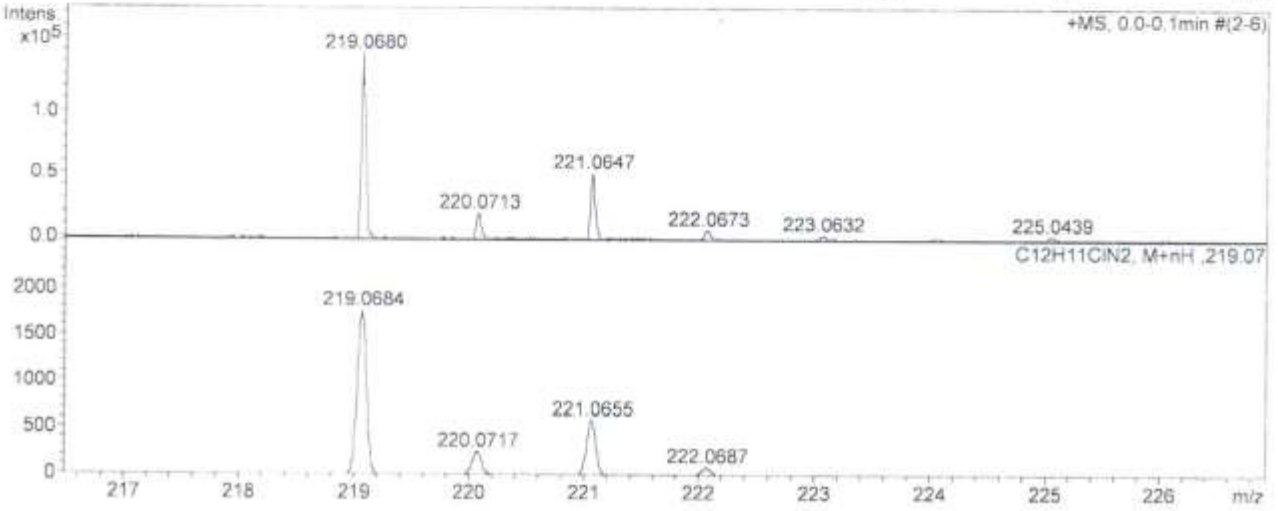
Analysis Name	D:\Data\FEB-2021\PCR\18022021_PCR_TN_1475.d	Acquisition Date	2/22/2021 11:05:34 AM
Method	Pos_tune_low.m	Operator	Amit S.Sahu
Sample Name	Tmix-131118	Instrument	micrOTOF-Q II 10337
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







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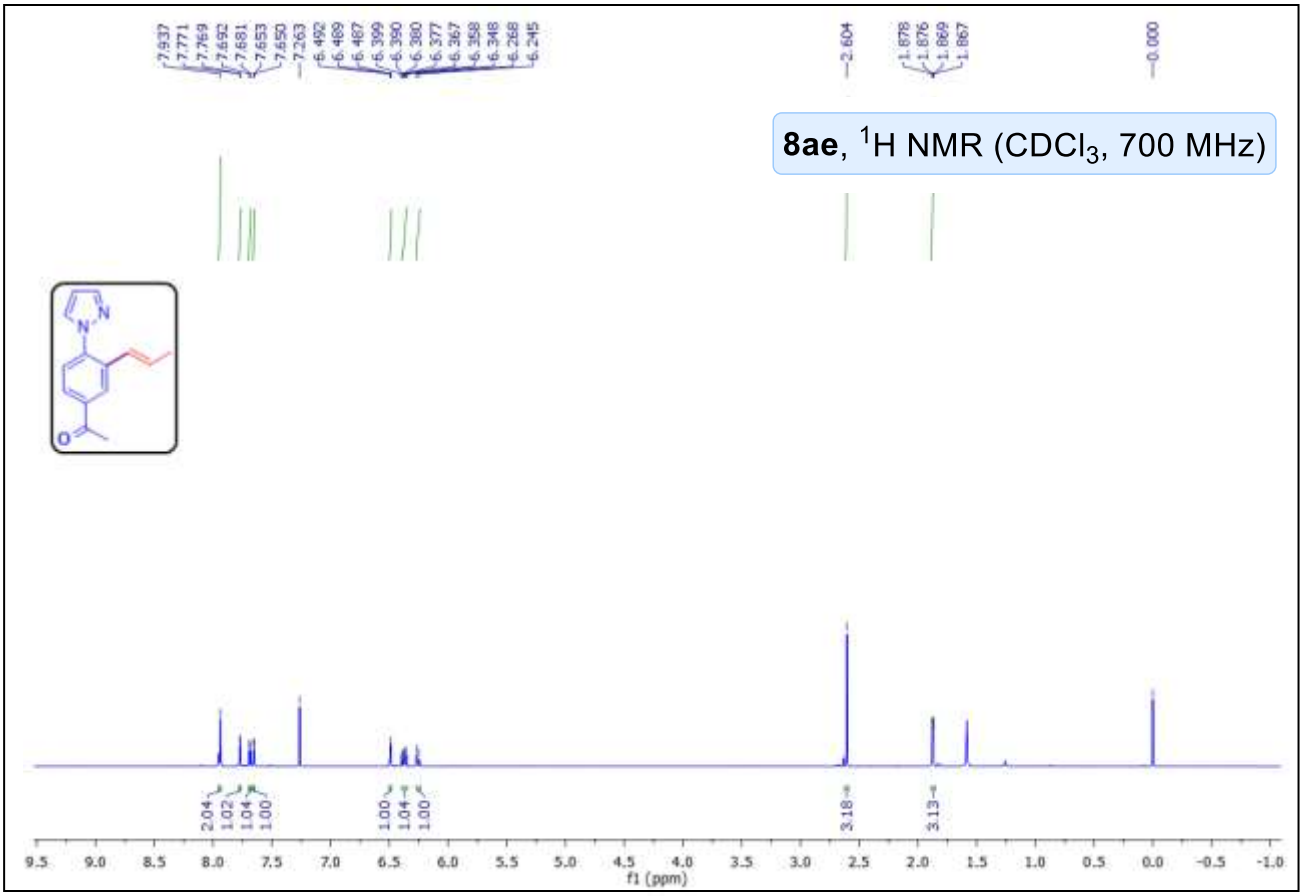
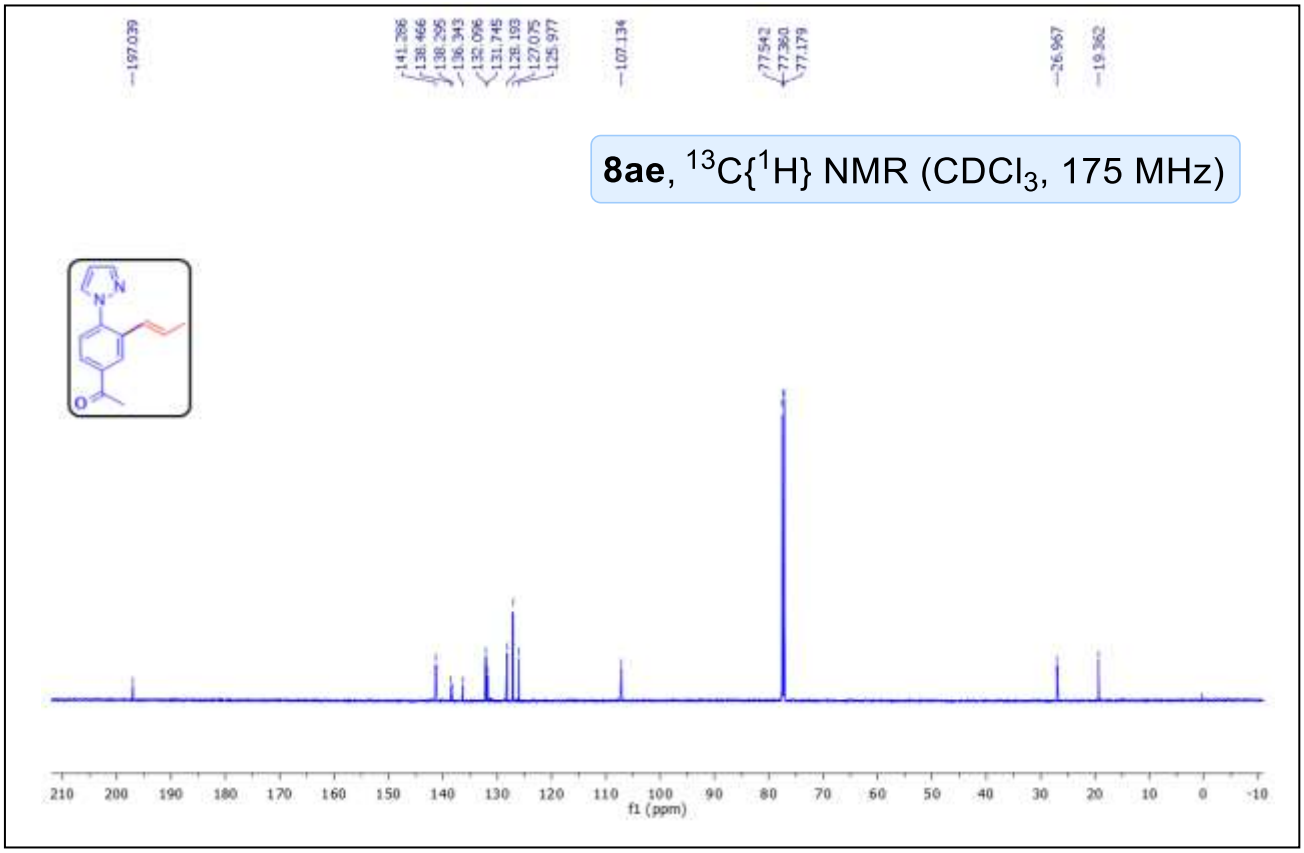

7.937
7.771
7.769
7.692
7.681
7.653
7.650
7.263
6.492
6.489
6.487
6.399
6.390
6.380
6.377
6.367
6.358
6.348
6.268
6.245
2.604
1.878
1.876
1.869
1.867
0.000
8ae, 1H NMR (CDCl3, 700 MHz)
2.04
1.02
1.04
1.00
1.00
1.04
1.00
3.18
3.13
f1 (ppm)


197.039
141.288
138.466
138.295
136.343
132.096
131.745
128.193
127.075
125.977
107.134
77.542
77.360
77.179
26.967
19.362
8ae, 13C{1H} NMR (CDCl3, 175 MHz)
f1 (ppm)

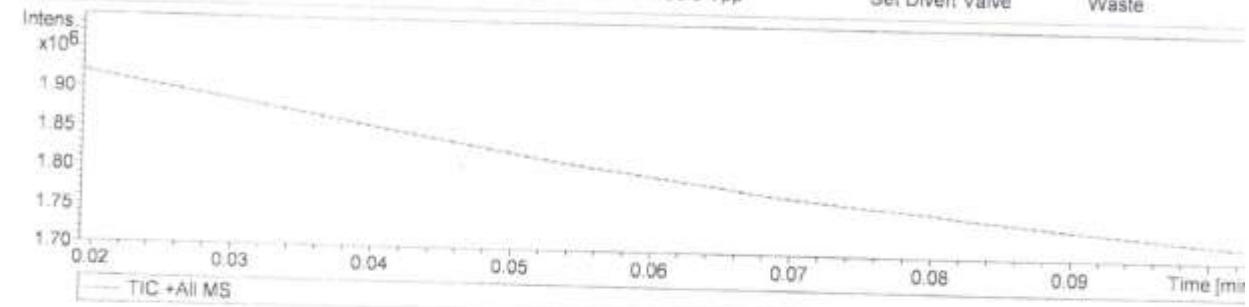
Display Report

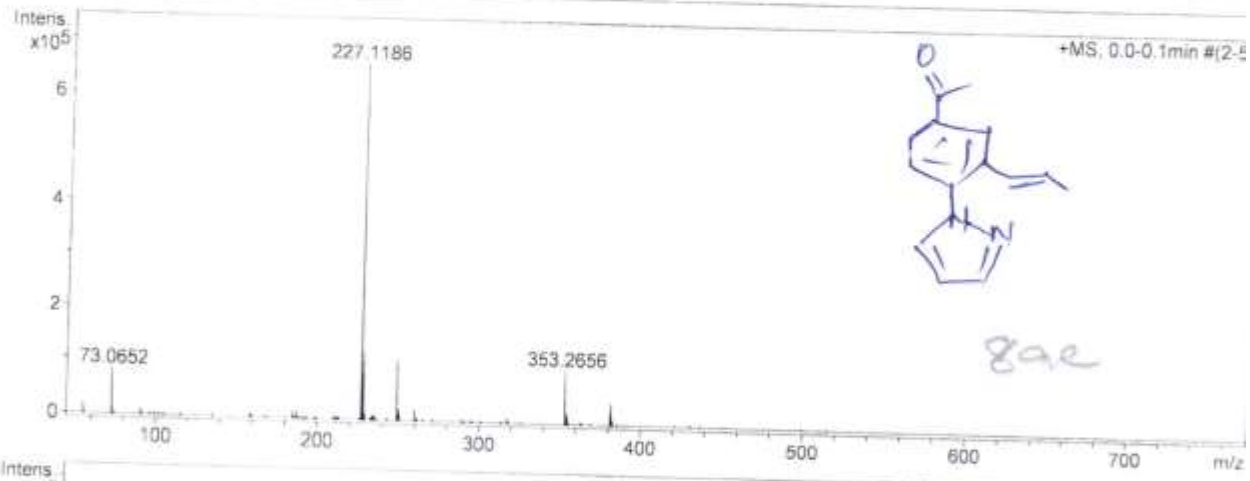
Analysis Info

Analysis Name	D:\Data\MAR-2021\PCR\02032021_PCR_TN_1496.d	Acquisition Date	3/2/2021 10:52:09 AM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	Amit S.Sahu
Comment		Instrument	micrOTOF-Q II 10337

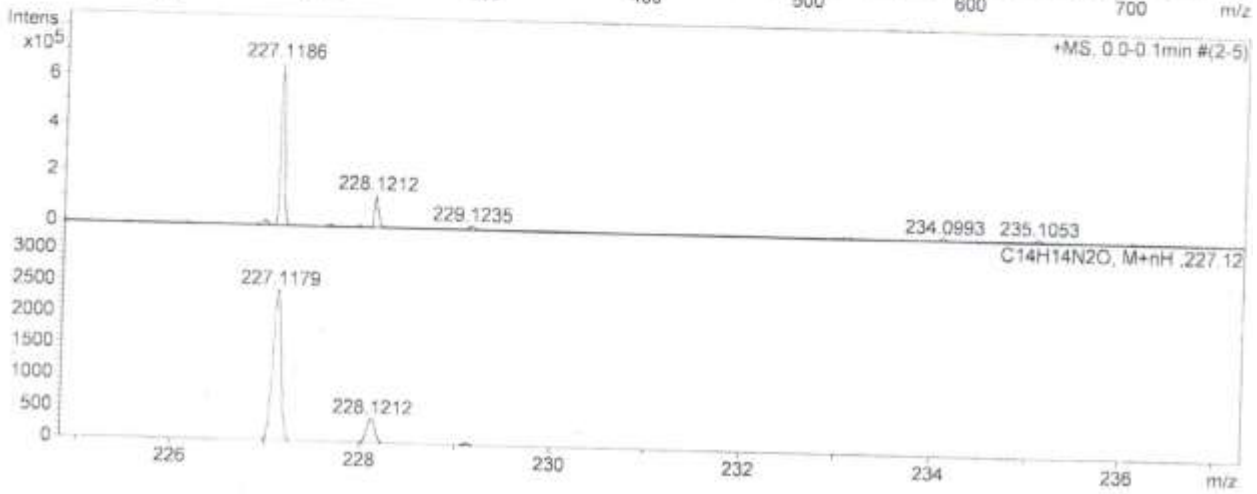
Acquisition Parameter

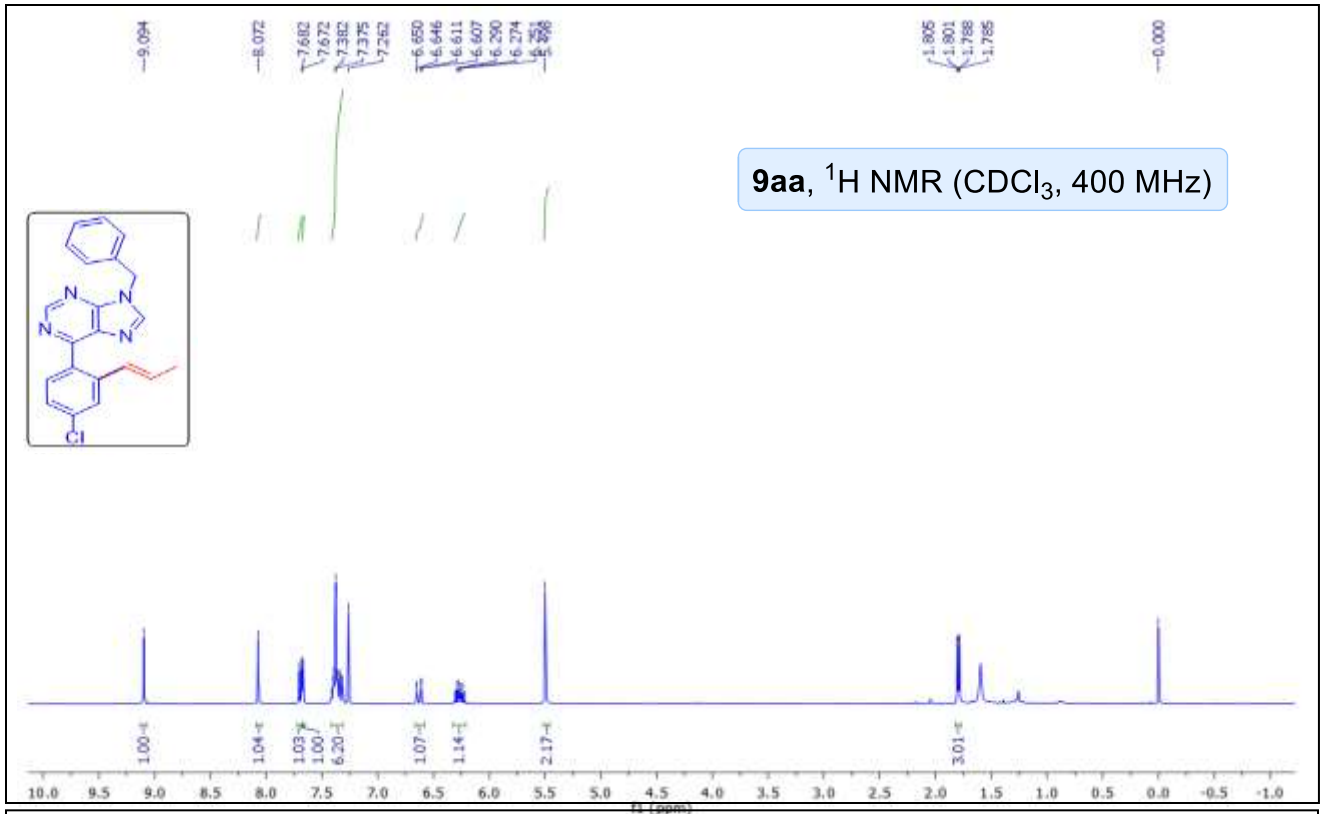
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste



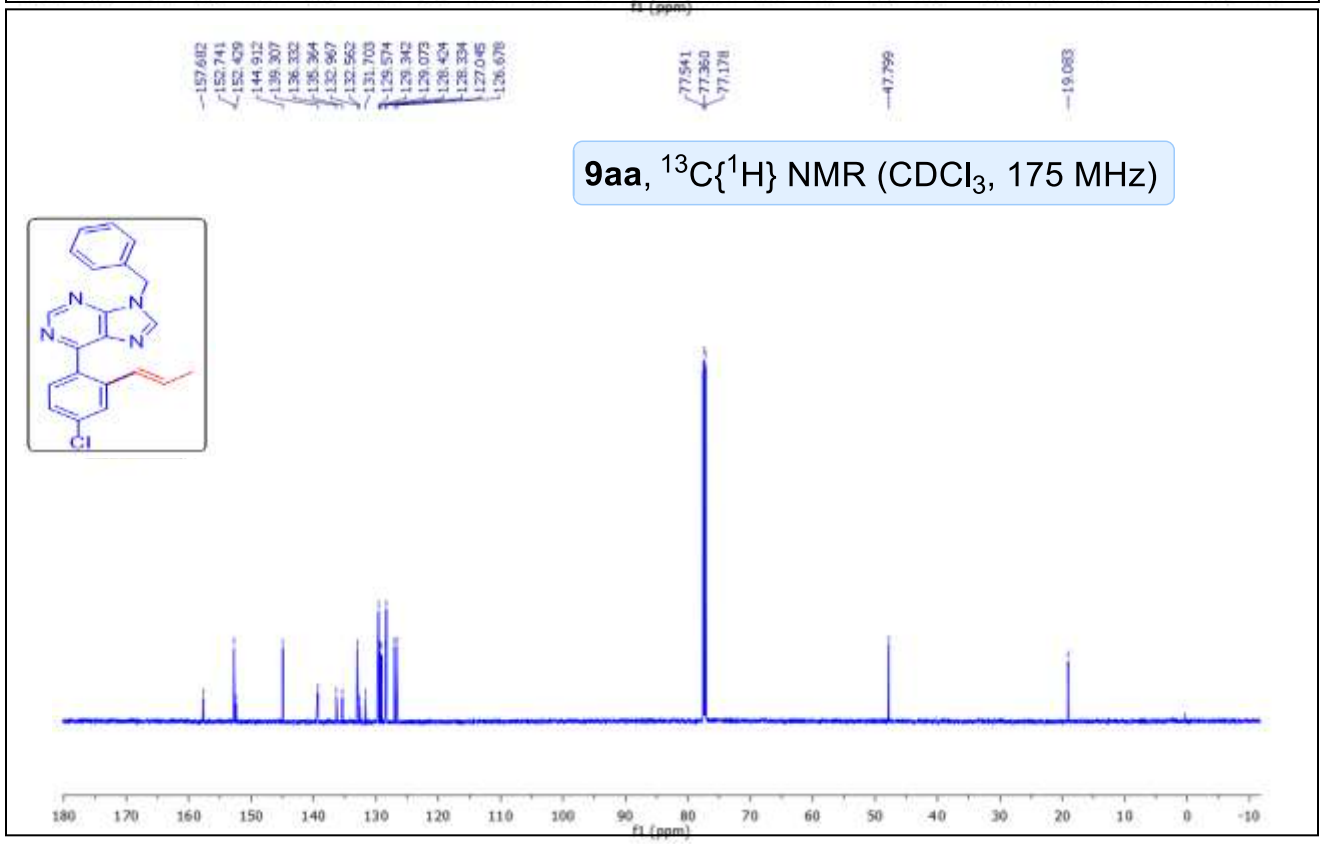


8ae





9aa, ^{1}H NMR ($CDCl_3$, 400 MHz)



9aa, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 175 MHz)

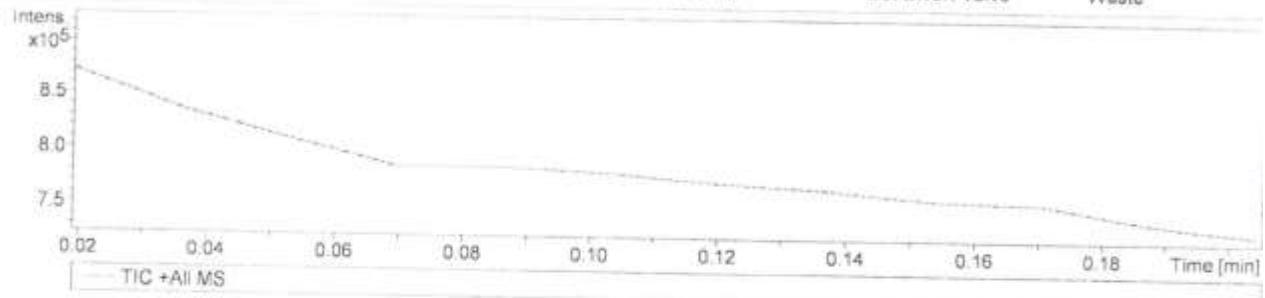
Display Report

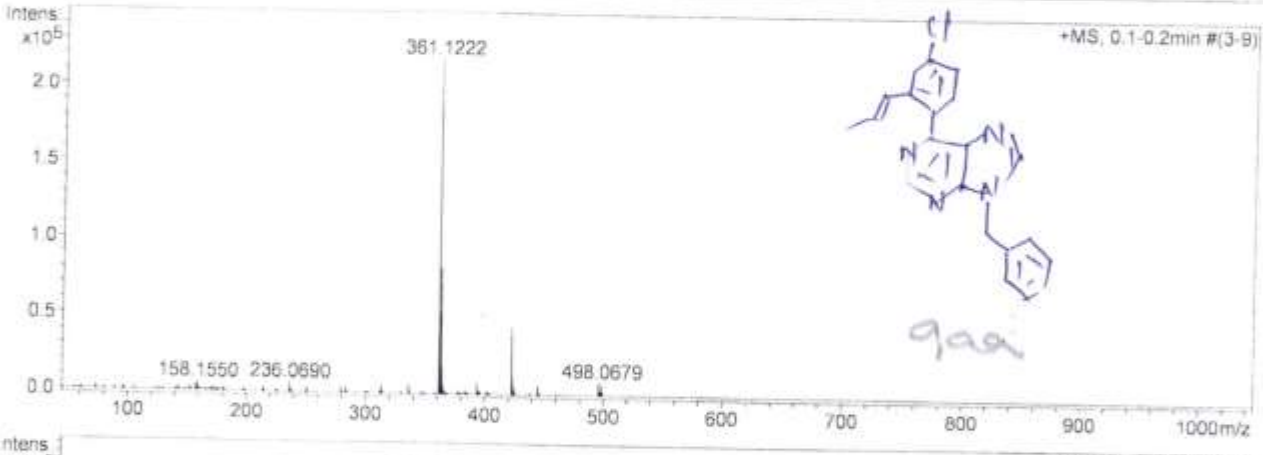
Analysis Info

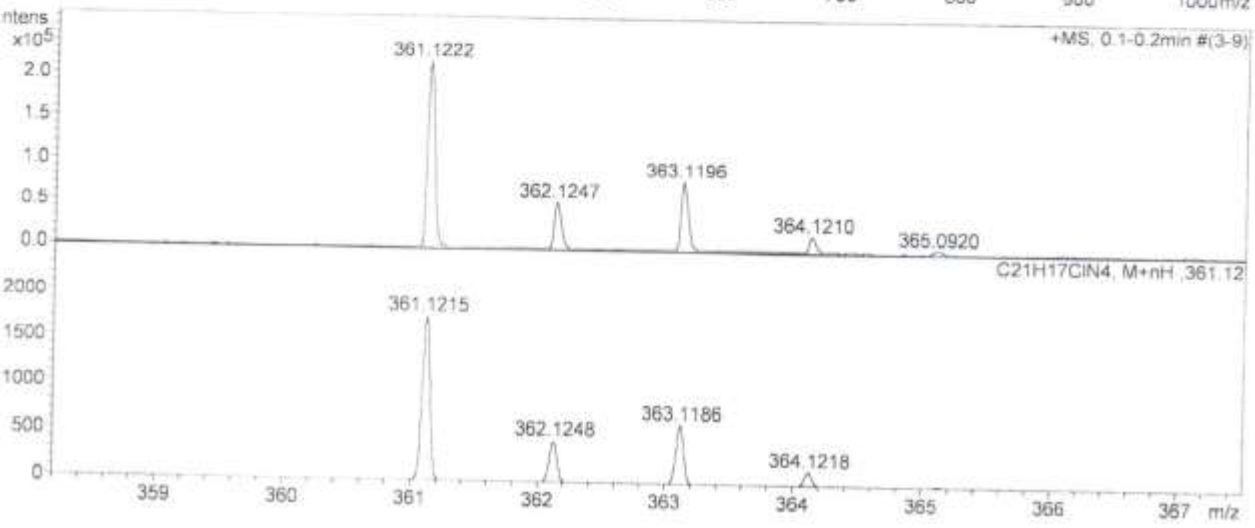
Analysis Name	D:\Data\MAR-2021\PCR\26032021_PCR_TN_1525.d	Acquisition Date	3/26/2021 11:19:21 AM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	Amit S.Sahu
Comment		Instrument	micrOTOF-Q II 10337

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







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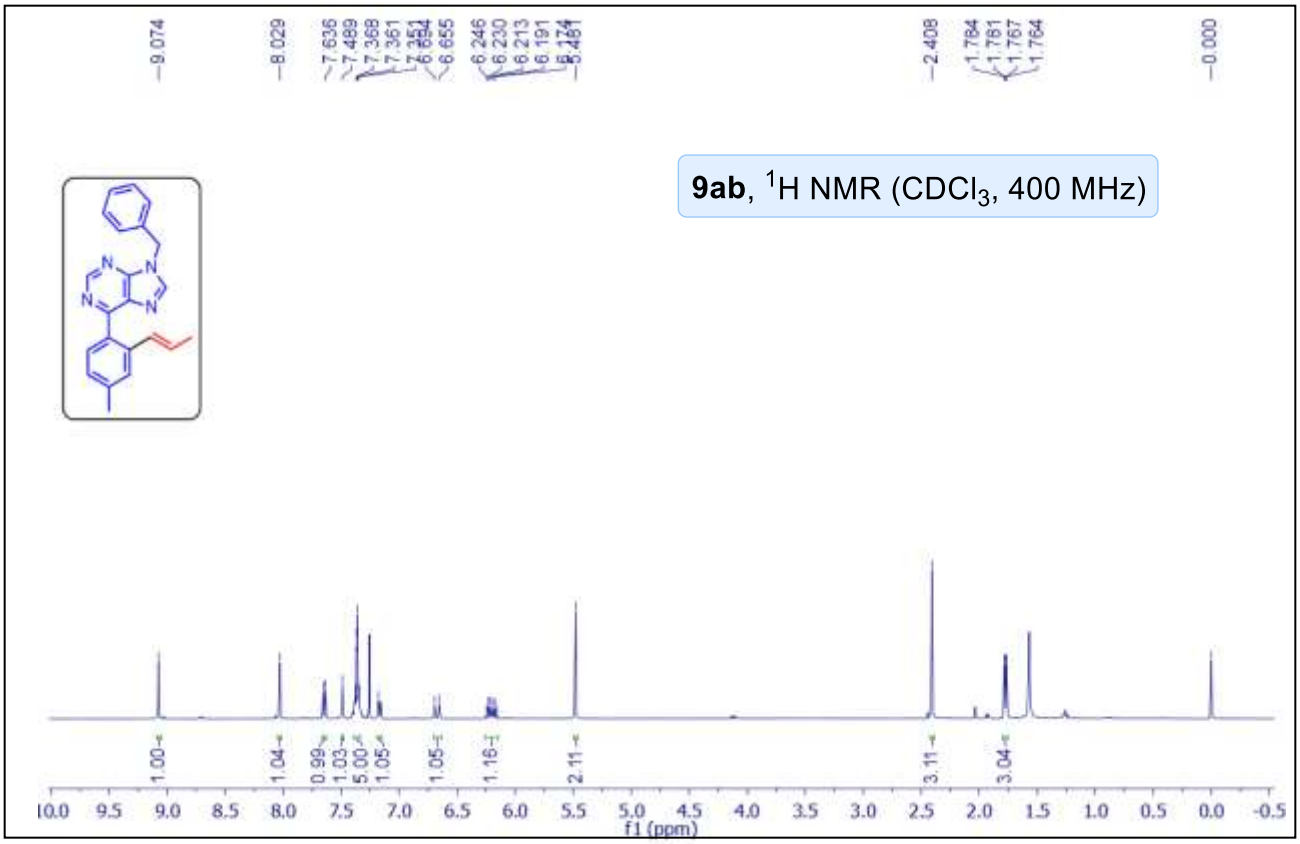
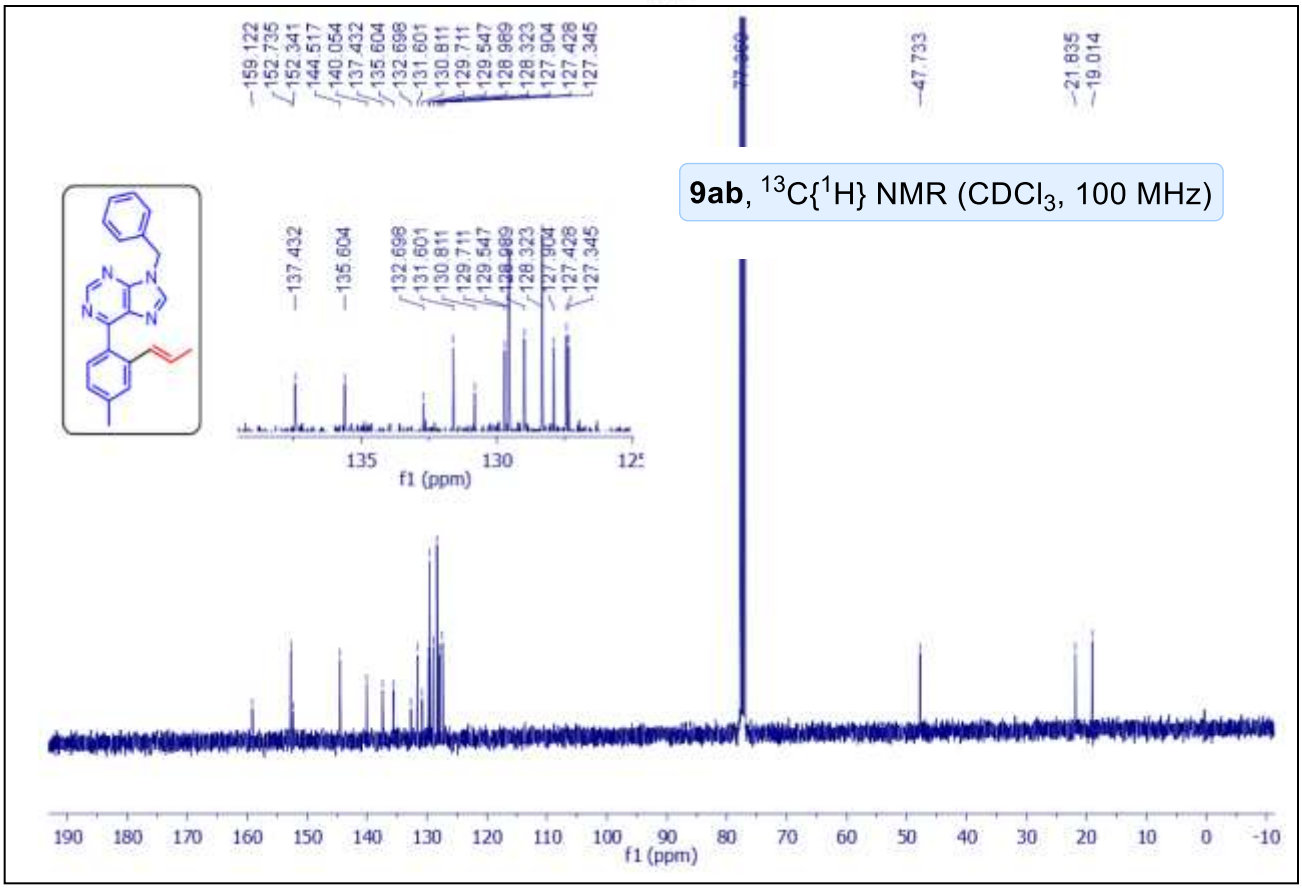


9ab, ^{1}H NMR ($CDCl_3$, 400 MHz)



9ab, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)

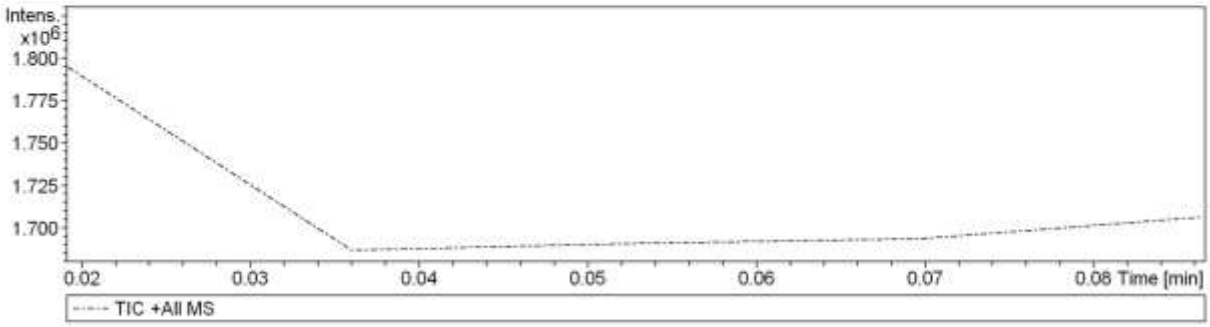
Display Report

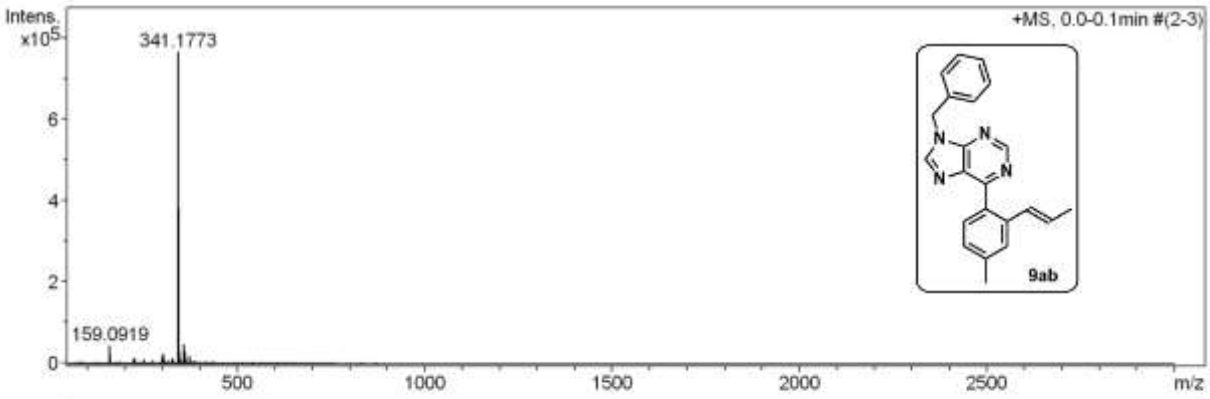
Analysis Info

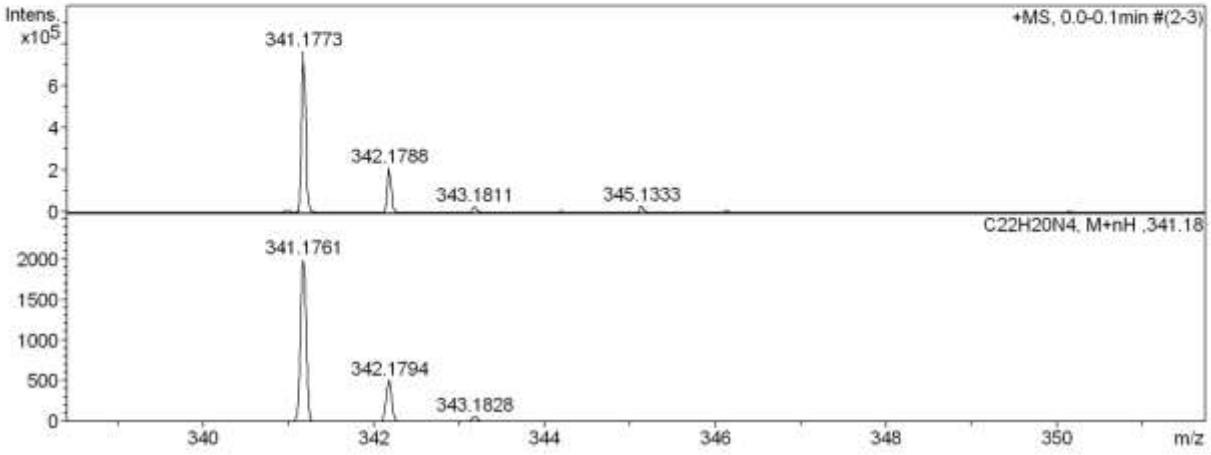
Analysis Name	D:\Data\NOV-2021\PCR\29112021_PCR_TN_2214.d	Acquisition Date	11/29/2021 11:38:43 AM
Method	Pos_tune_low.m	Operator	Amit S.Sahu
Sample Name	Tmix-131118	Instrument	micrOTOF-Q II 10337
Comment			

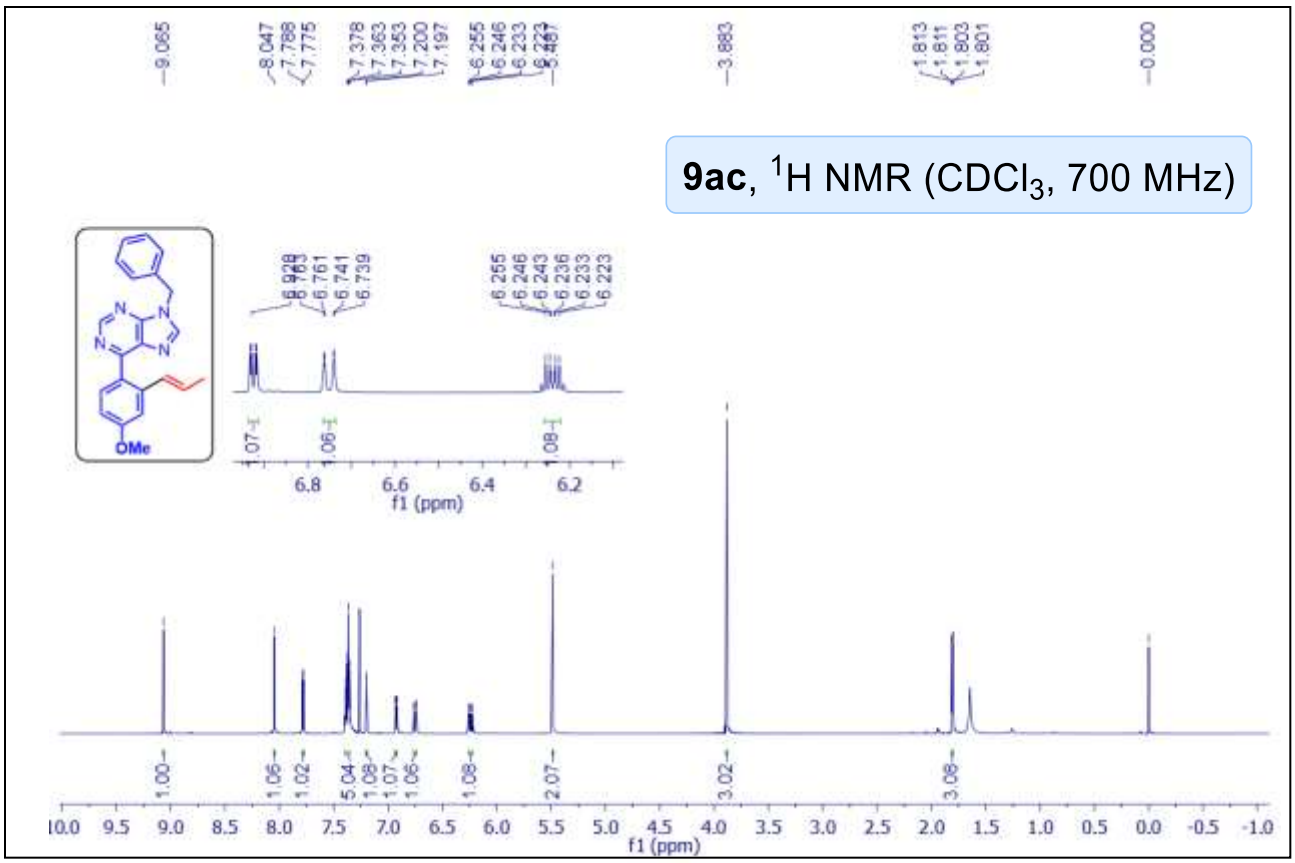
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

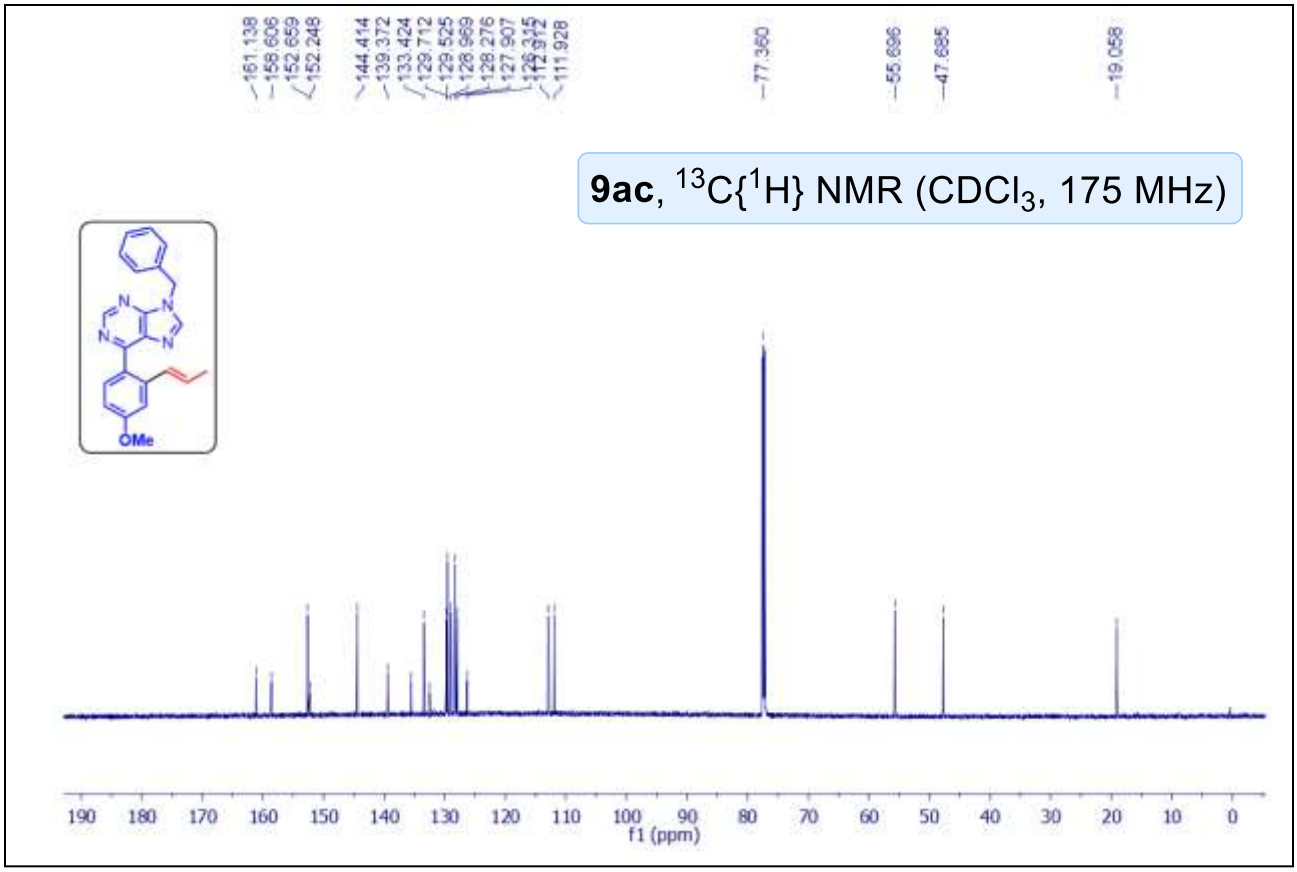








9ac, ^{1}H NMR ($CDCl_3$, 700 MHz)



9ac, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 175 MHz)

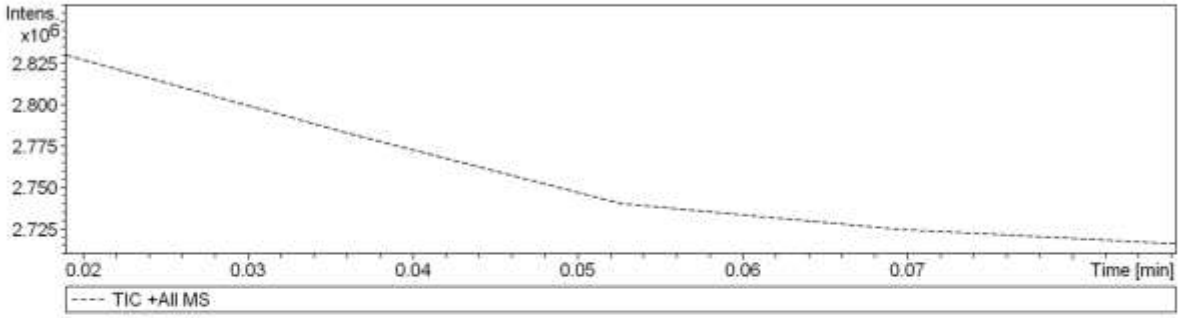
Display Report

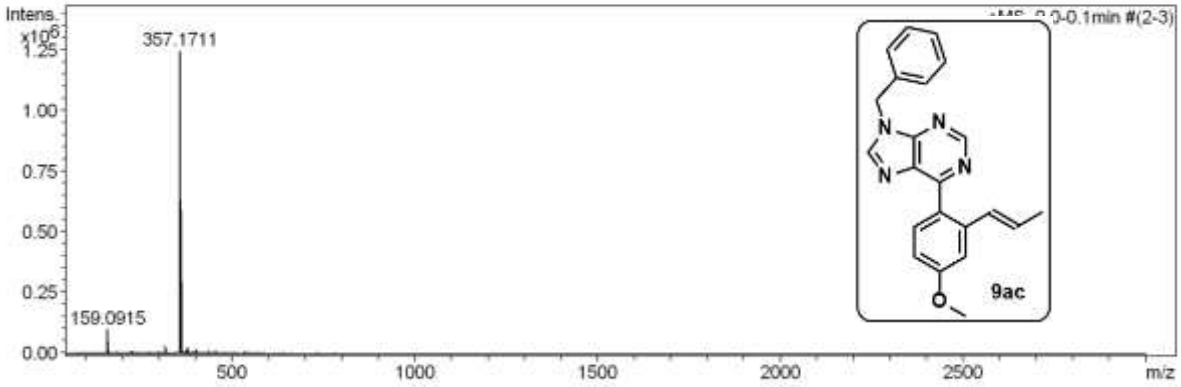
Analysis Info

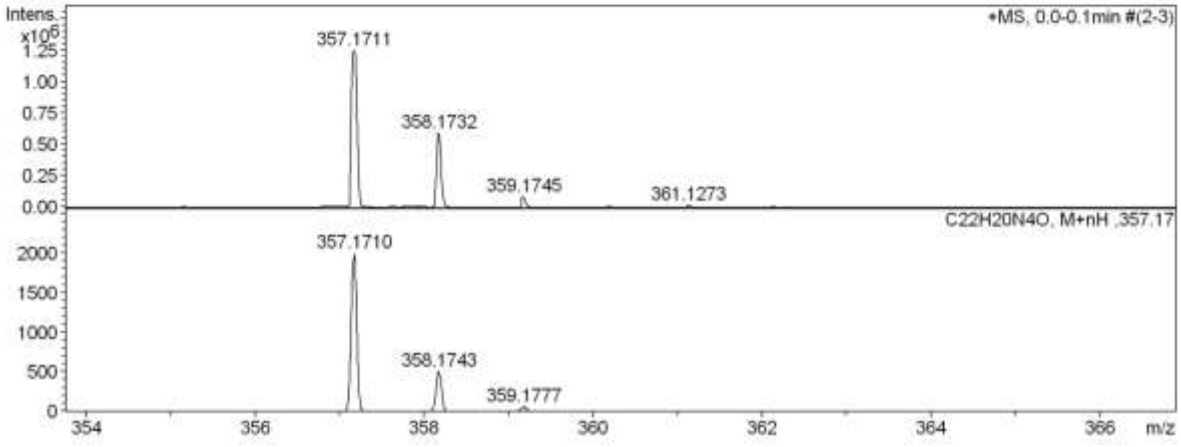
Analysis Name	D:\Data\NOV-2021\PCR\29112021_PCR_TN_2198.d	Acquisition Date	11/29/2021 11:35:23 AM
Method	Pos_tune_low.m	Operator	Amit S.Sahu
Sample Name	Tmix-131118	Instrument	micrOTOF-Q II 10337
Comment			

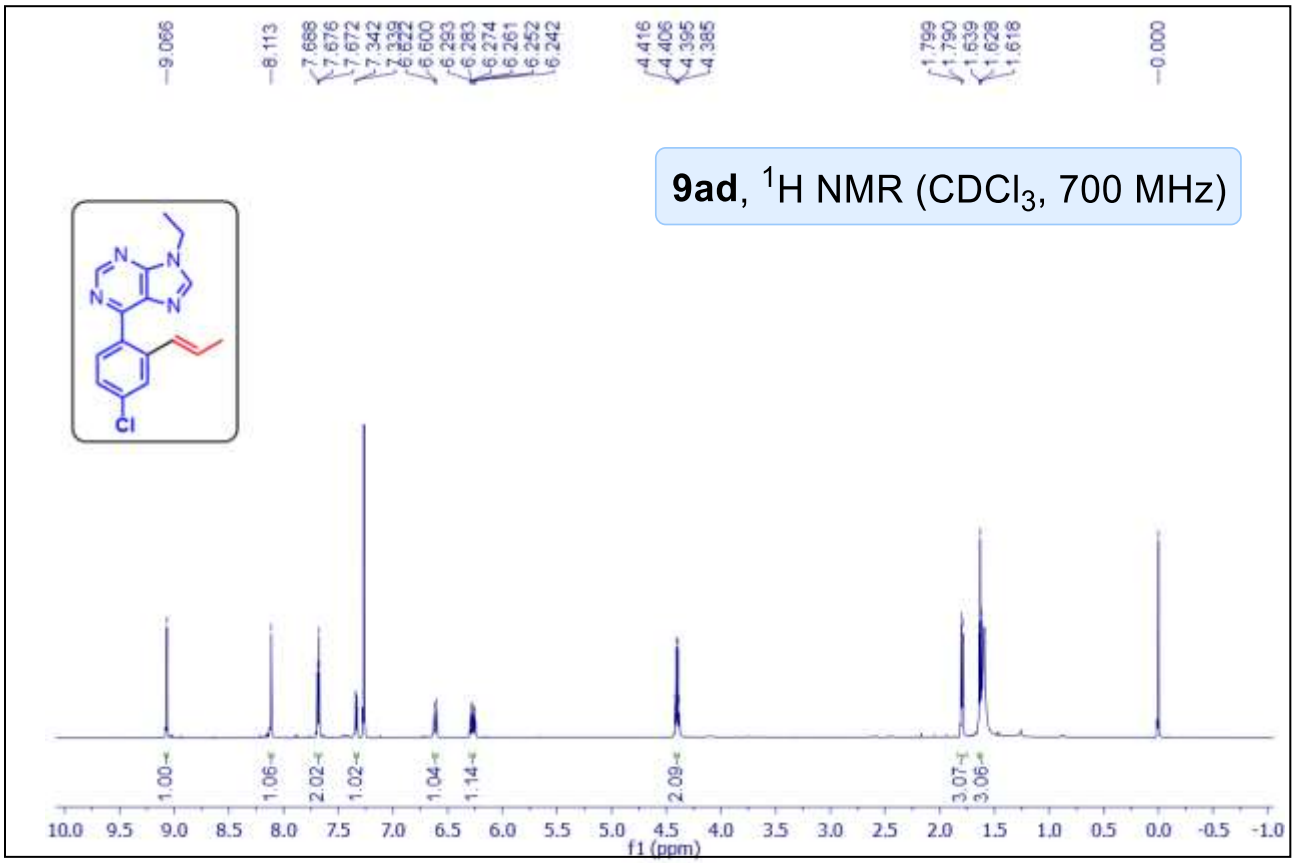
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

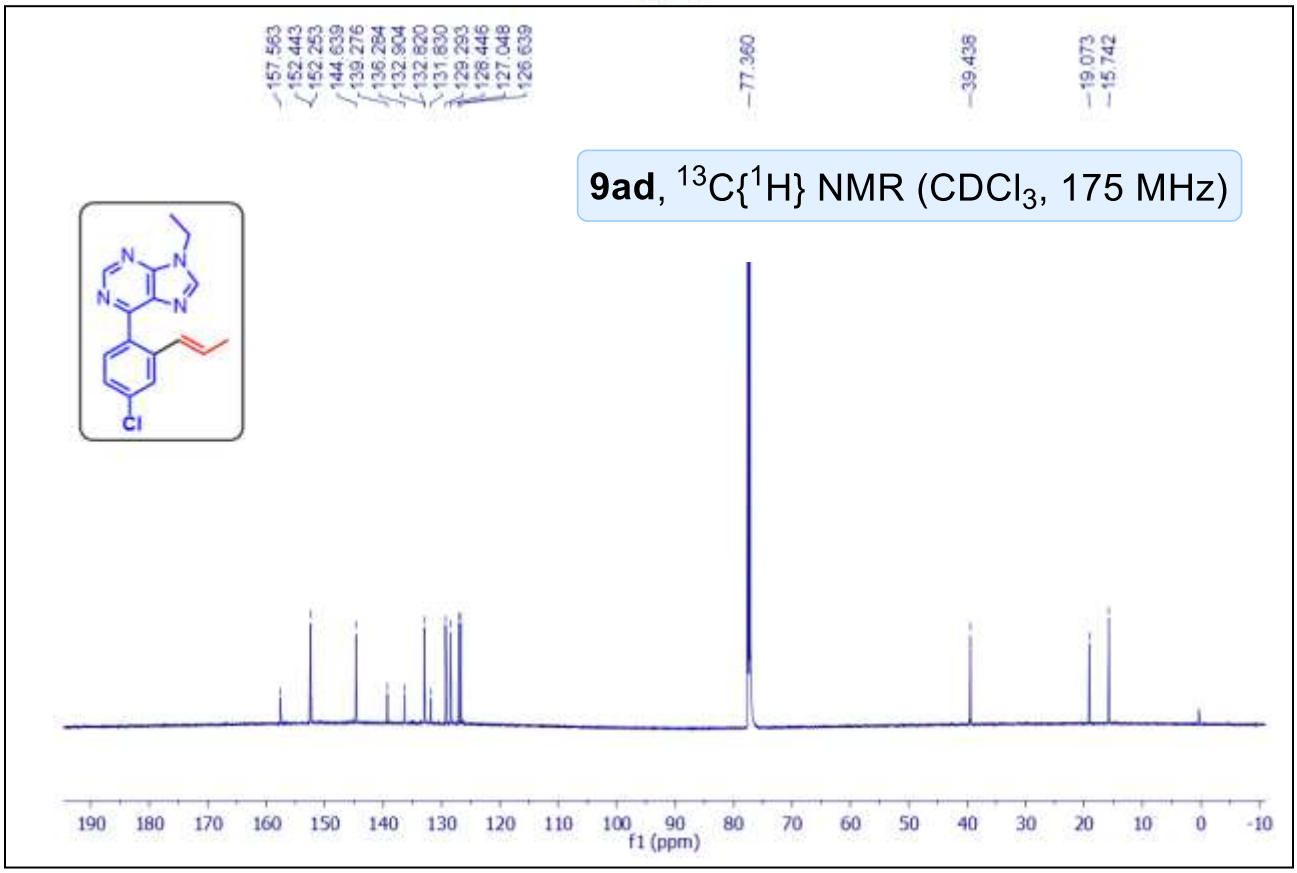








9ad, ^{1}H NMR ($CDCl_3$, 700 MHz)



9ad, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 175 MHz)

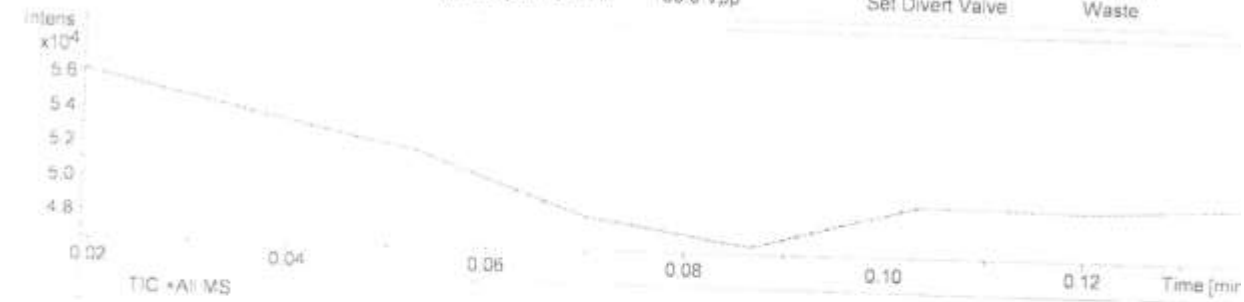
Display Report

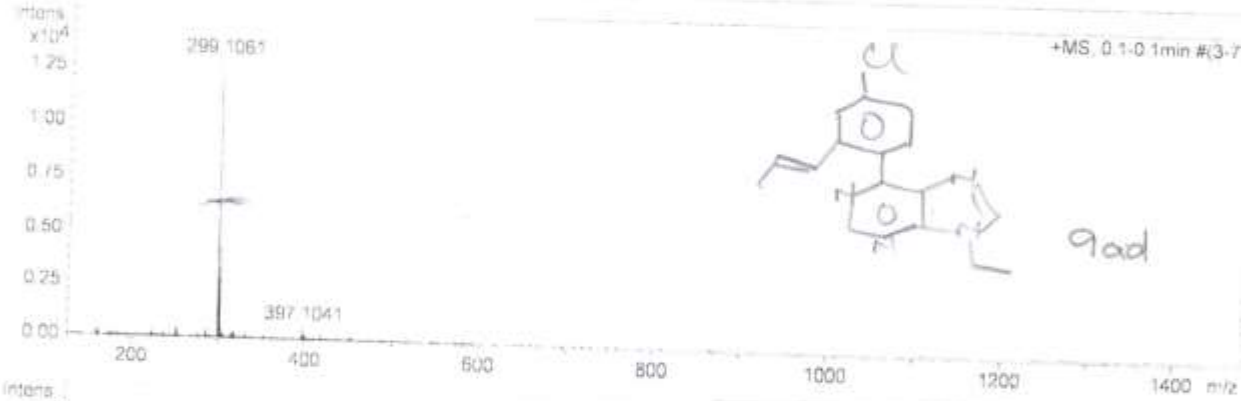
Analysis Info

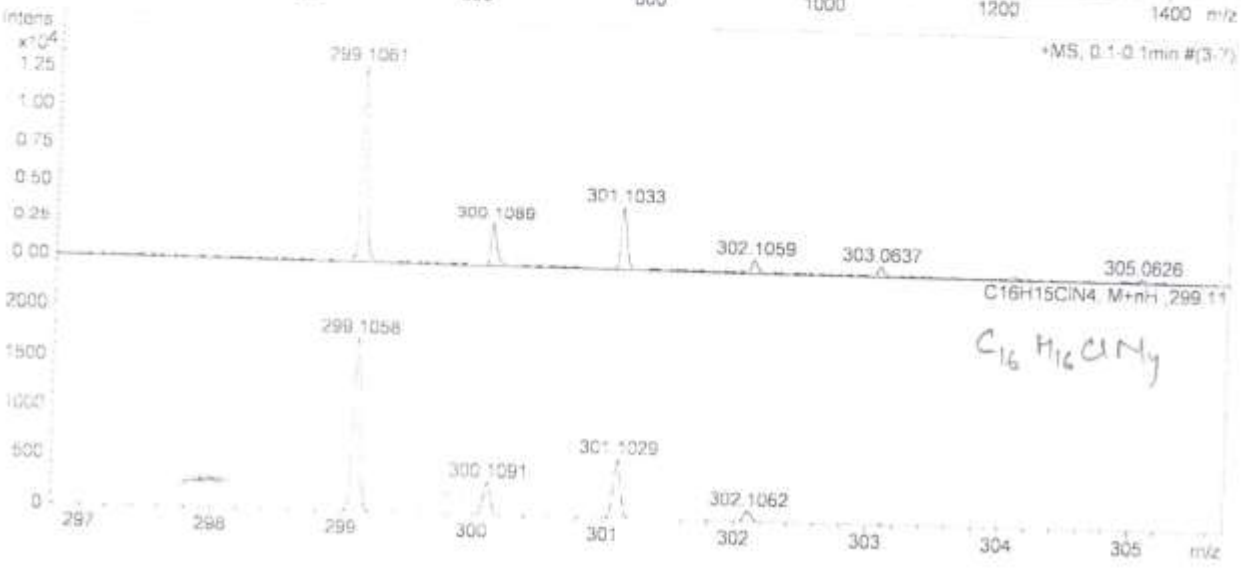
Analysis Name	D:\Data\NOV-2021\PCR\29112021_PCR_TN_2216.d	Acquisition Date	11/29/2021 3:18:42 PM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	Amit S.Sahu
Comment		Instrument	micrOTOF-Q II 10337

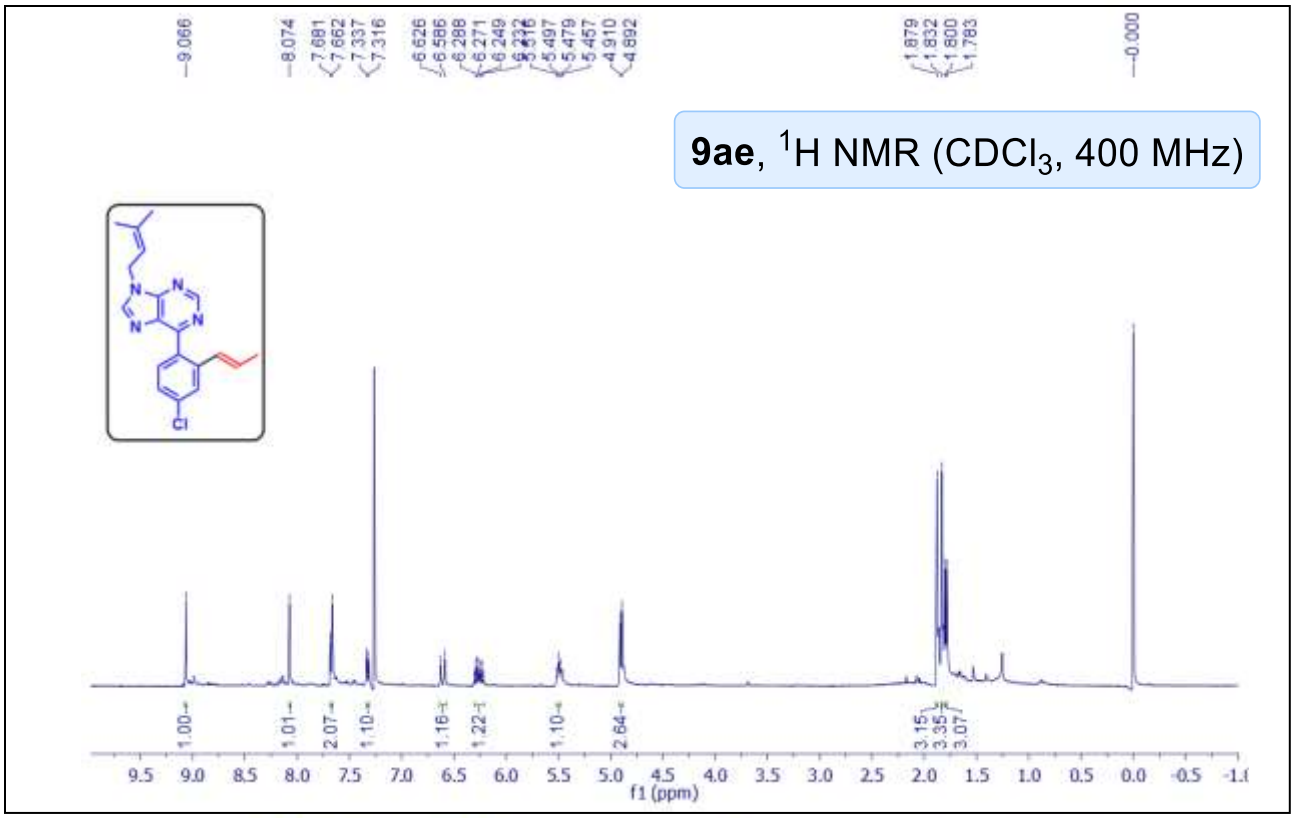
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

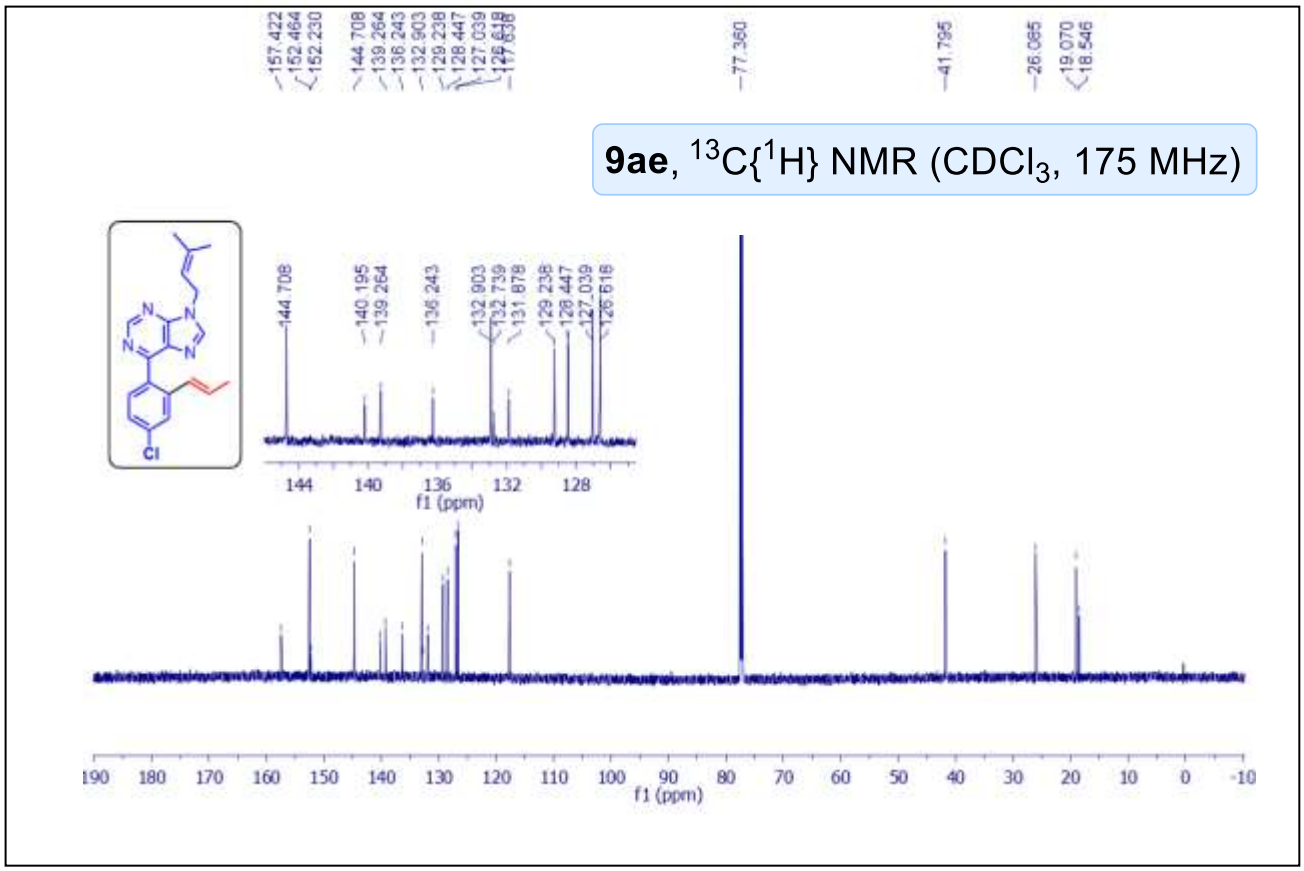








9ae, ^{1}H NMR ($CDCl_3$, 400 MHz)



9ae, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 175 MHz)

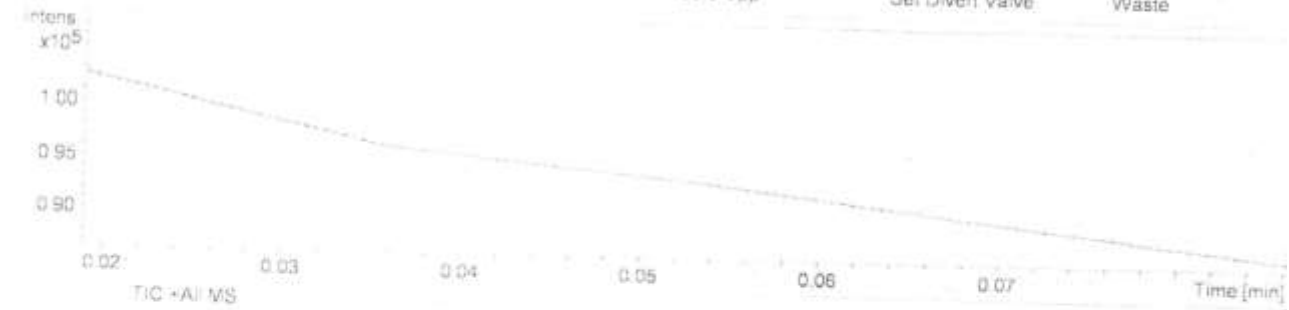
Display Report

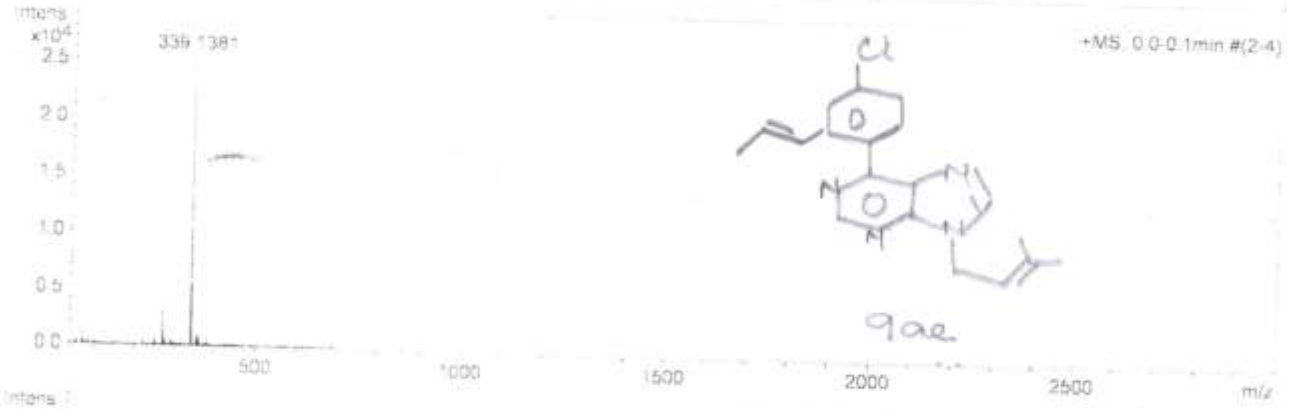
Analysis Info

Analysis Name	D:\Data\NOV-2021\PCR\29112021_PCR_TN_2218.d	Acquisition Date	11/29/2021 3:24:53 PM
Method	Pos_tune_low.m		
Sample Name	Tmx-HS1118	Operator	Amit S.Sahu
Comment		Instrument	micrOTOF-Q II 10337

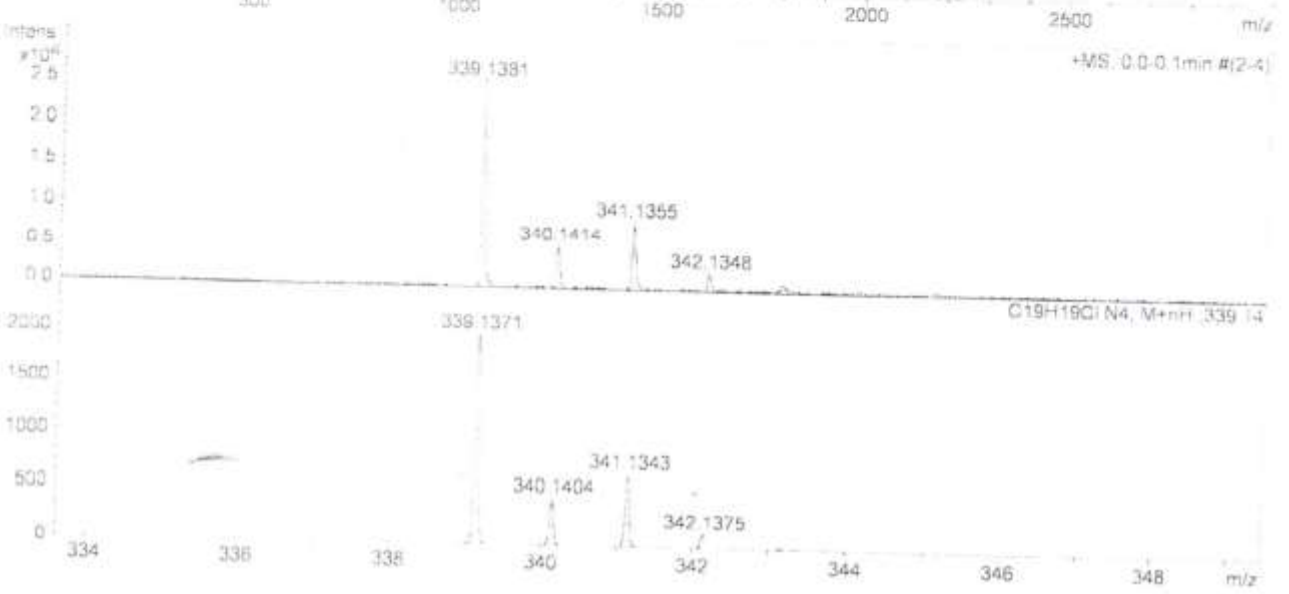
Acquisition Parameter

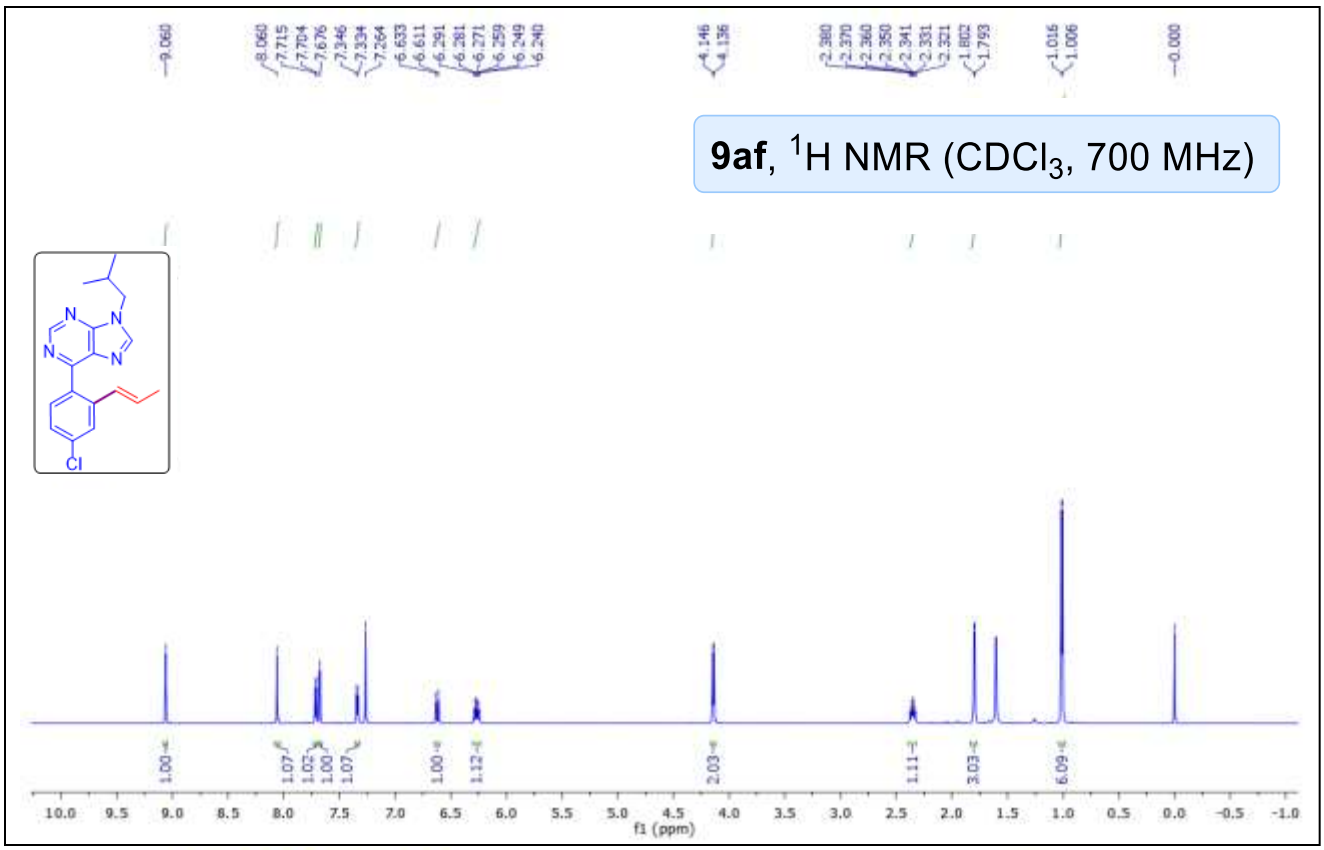
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

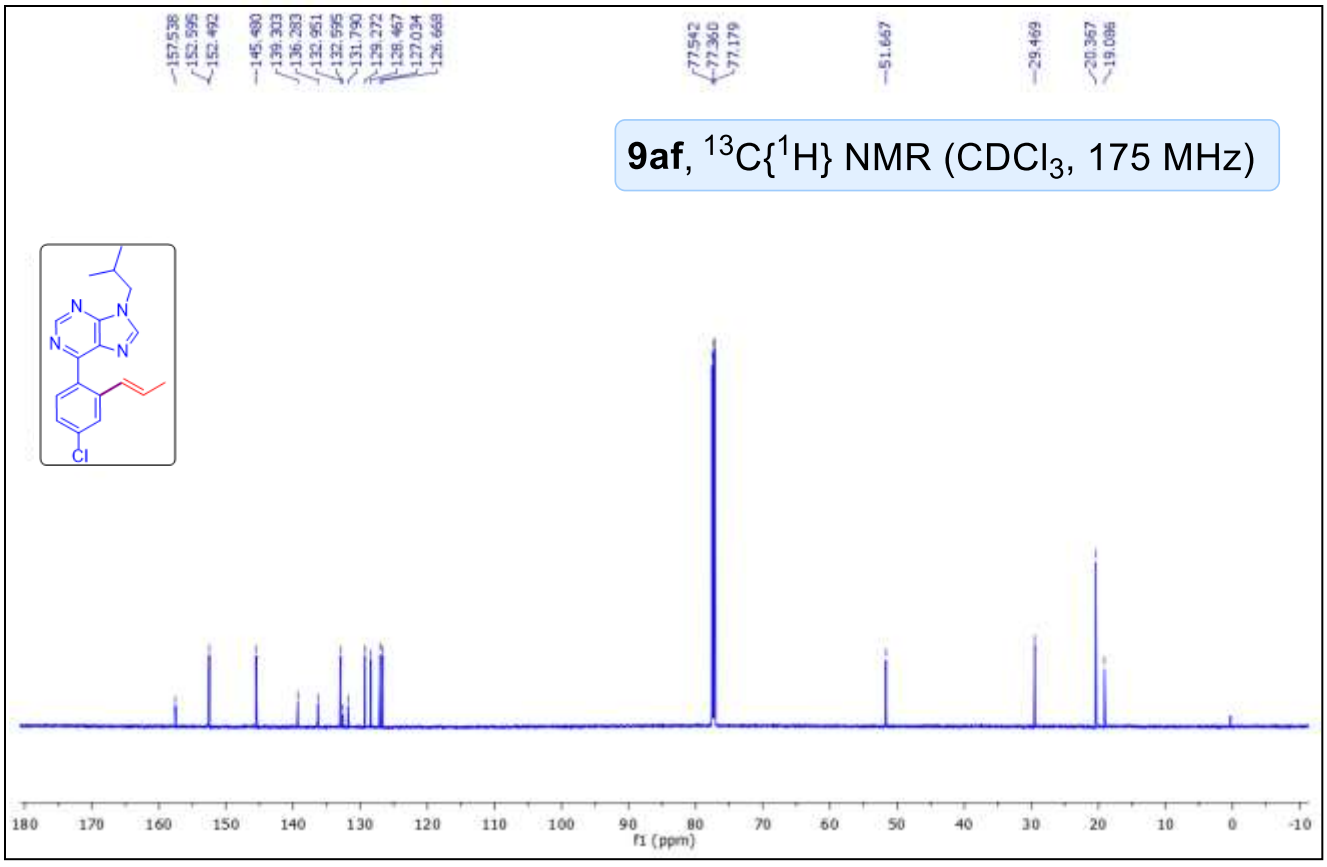




9ae




9af, ^{1}H NMR ($CDCl_3$, 700 MHz)
f1 (ppm)


9af, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 175 MHz)
f1 (ppm)

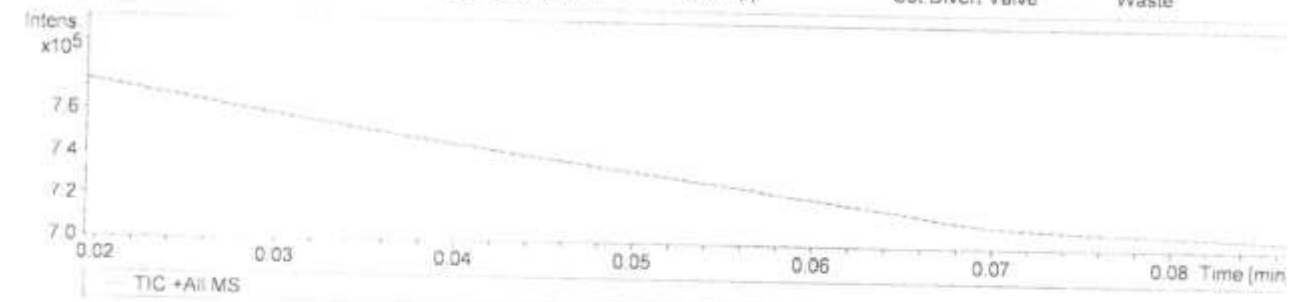
Display Report

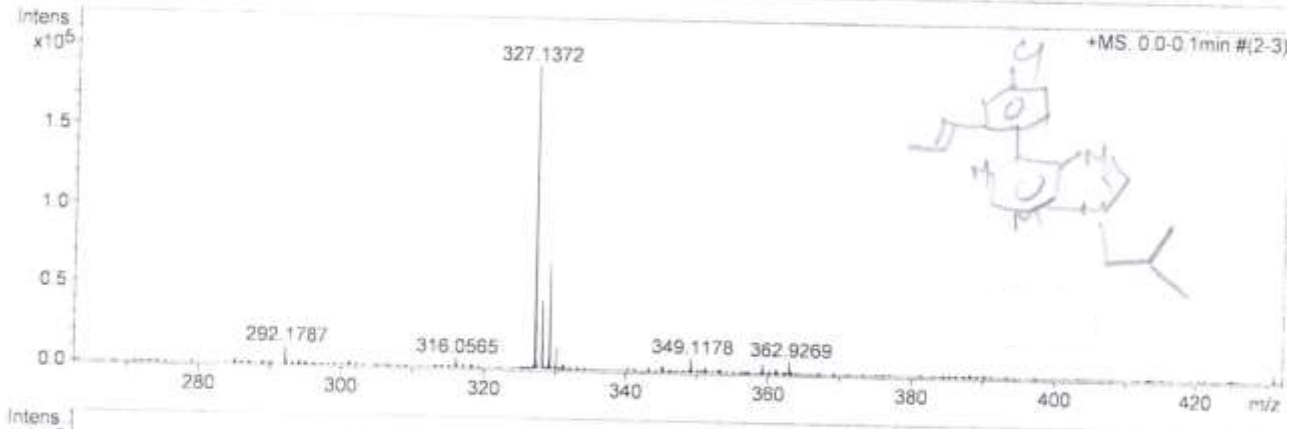
Analysis Info

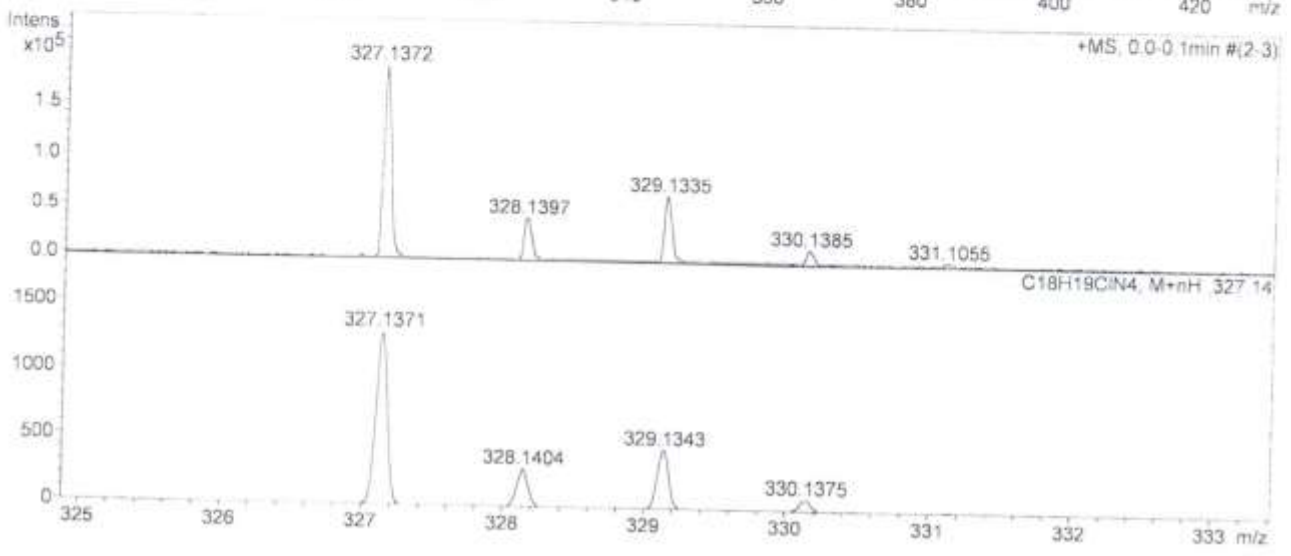
Analysis Name	D:\Data\MAR-2021\PCR\31032021_PCR_TN_1532B.d	Acquisition Date	3/31/2021 10:42:26 AM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	Amit S.Sahu
Comment		Instrument	micrOTOF-Q II 10337

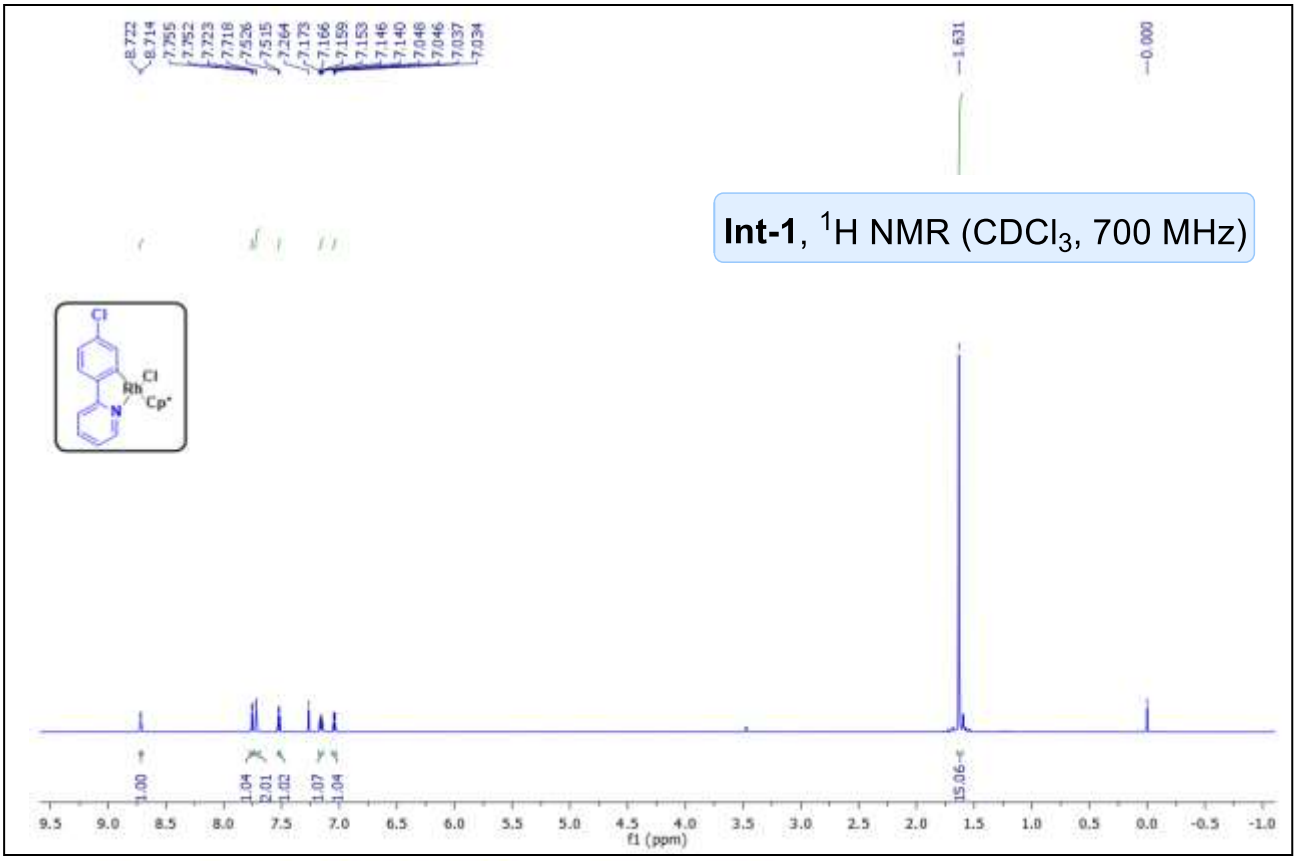
Acquisition Parameter

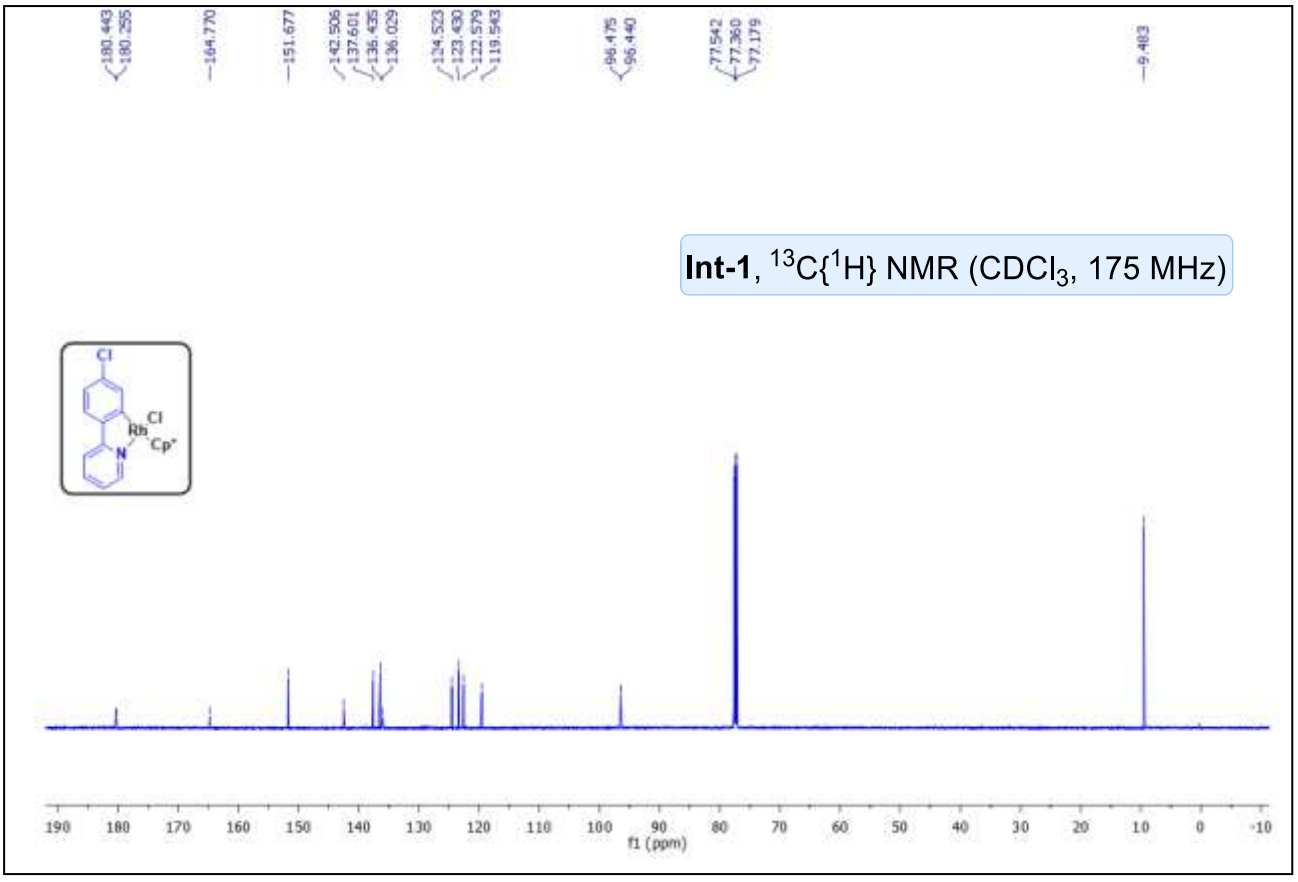
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste

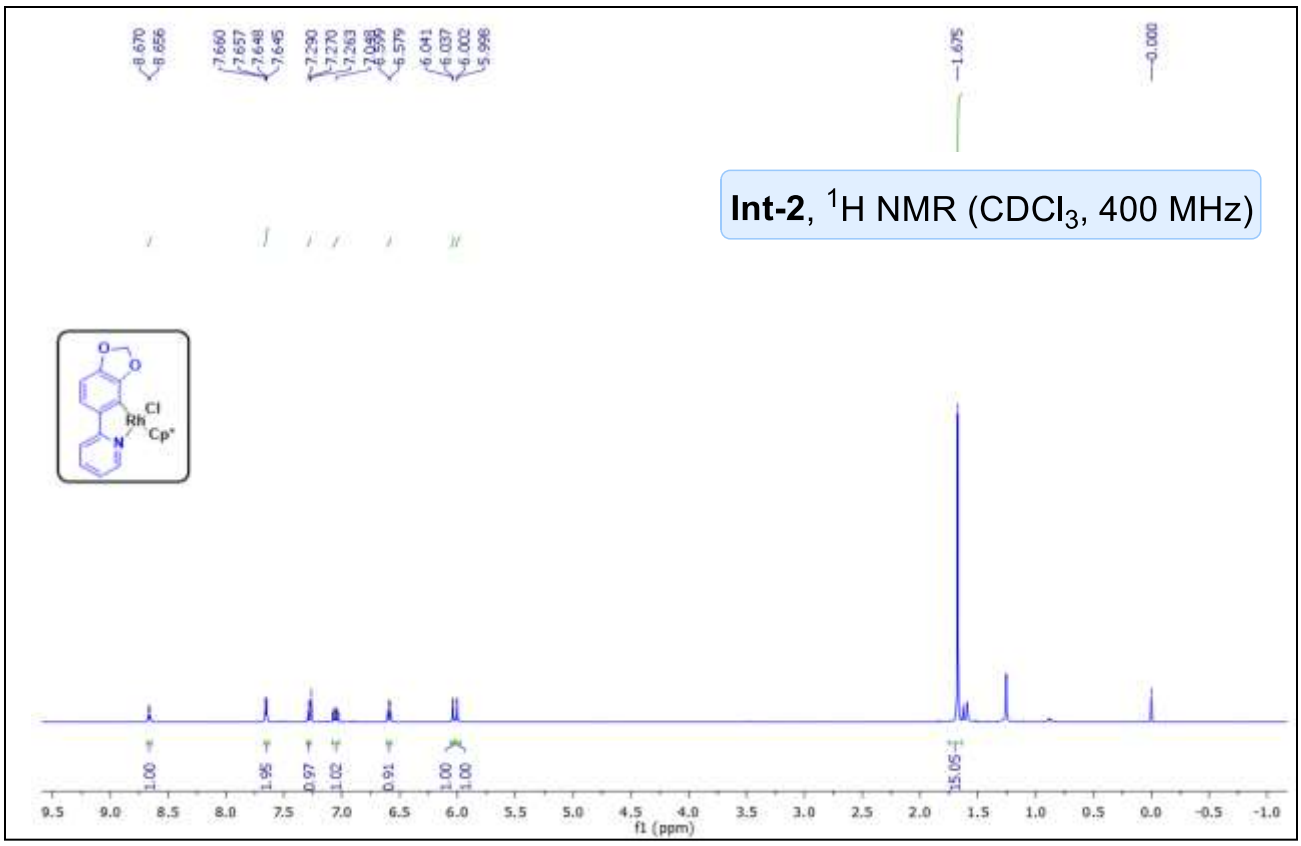


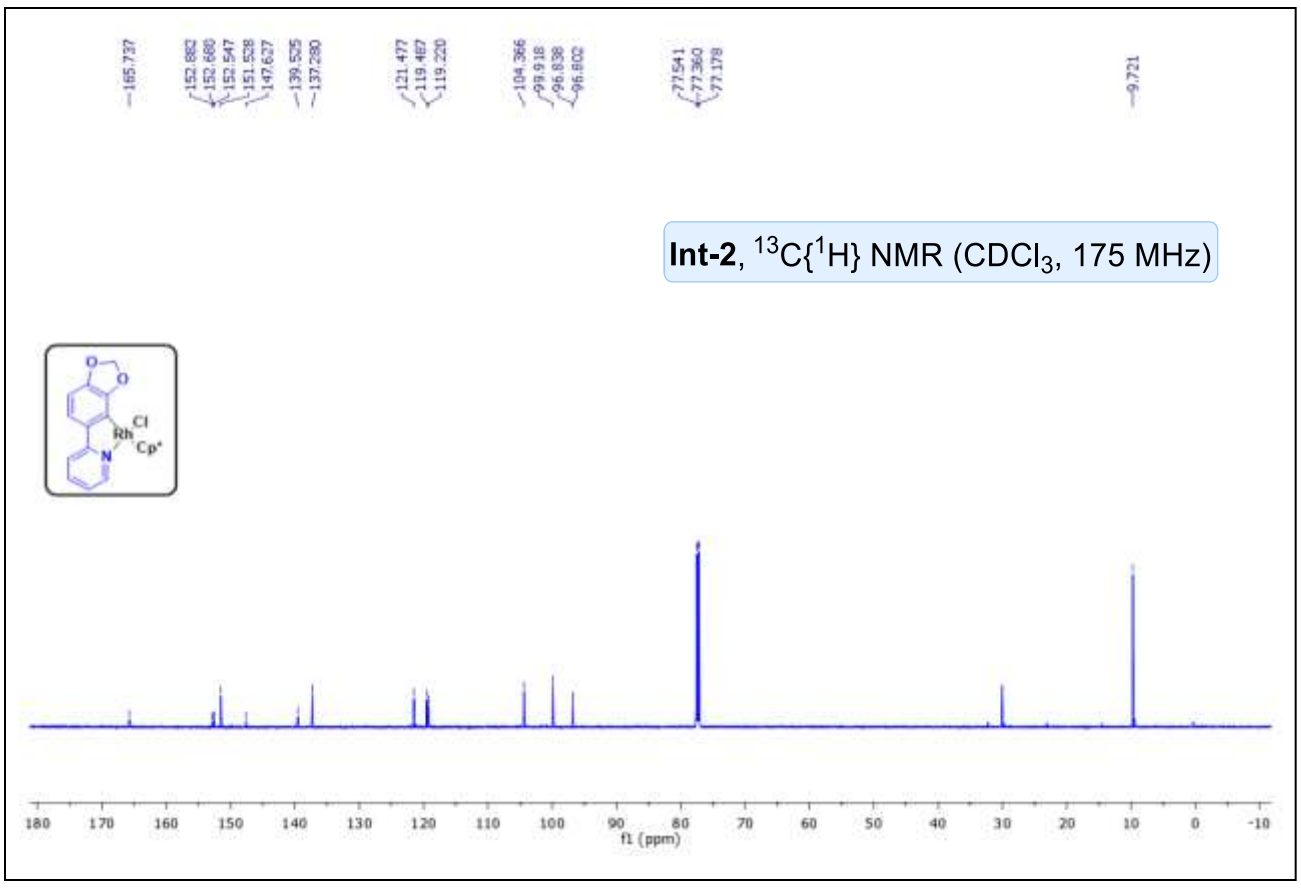





Int-1, ^{1}H NMR ($CDCl_3$, 700 MHz)
f1 (ppm)


Int-1, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 175 MHz)
f1 (ppm)


8.670
8.656
7.660
7.657
7.648
7.645
7.290
7.270
7.263
7.048
6.579
6.041
6.037
6.002
5.998
1.675
0.000
Int-2, 1H NMR (CDCl3, 400 MHz)
Cl
Rh
Cp*
N
1.00
1.95
0.97
1.02
0.91
1.00
1.00
15.05
f1 (ppm)


165.737
152.882
152.680
152.547
151.528
147.637
139.525
137.280
121.477
119.487
119.220
104.366
98.918
96.838
96.802
77.541
77.360
77.178
9.721
Int-2, 13C{1H} NMR (CDCl3, 175 MHz)
Cl
Rh
Cp*
N
f1 (ppm)

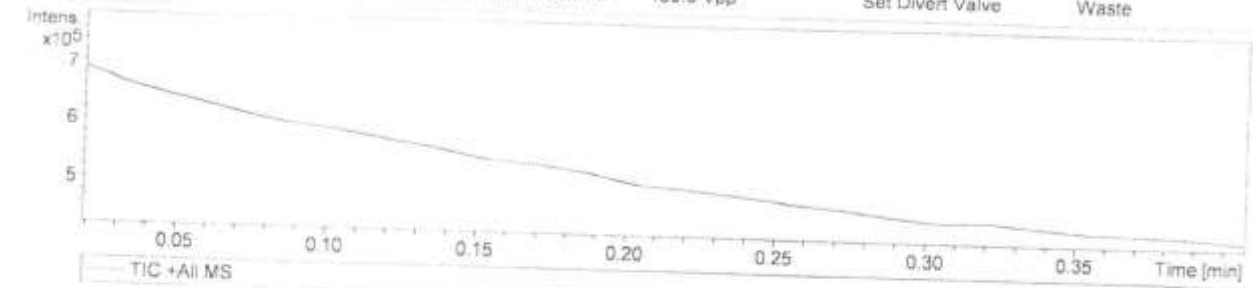
Display Report

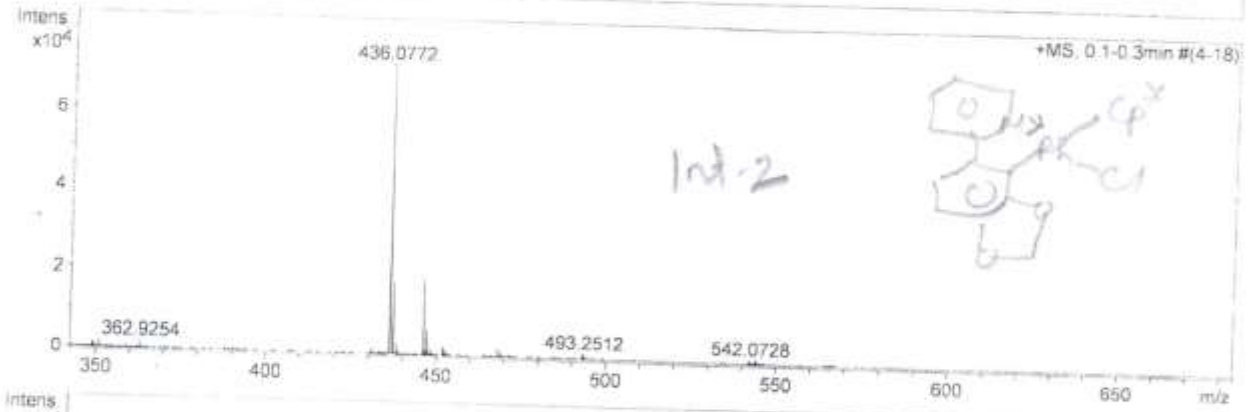
Analysis Info

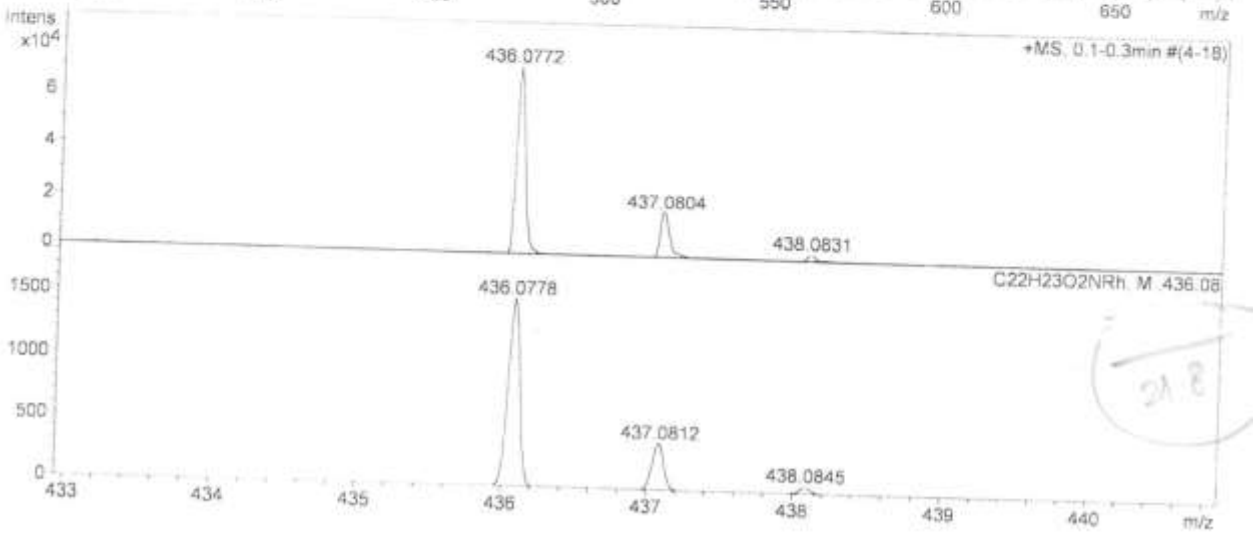
Analysis Name	D:\Data\MAR-2021\PCR\31032021_PCR_TN_1548.d	Acquisition Date	3/31/2021 10:46:47 AM
Method	Pos_tune_low.m		
Sample Name	Tmix-131118	Operator	Amit S Sahu
Comment		Instrument	micrOTOF-Q II 10337

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	130.0 Vpp	Set Divert Valve	Waste







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8. Crystallographic data:

(a) Crystals of the compounds **9af ((*E*)-6-(4-chloro-2-(prop-1-en-1-yl)phenyl)-9-isobutyl-9H-purine)** were obtained after slow evaporation of the mixture of DCM and MeOH. Crystals suited for single crystal X-Ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with a Rigaku Smartlab X-ray diffractometer equipped with graphite-monochromated (Cu-Kα radiation, λ = 1.54184, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT and SMART software packages and corrected for absorption with SADABS. The structure was solved by direct methods and refined on F2 with SHELXL-97 using Olex-2 software.

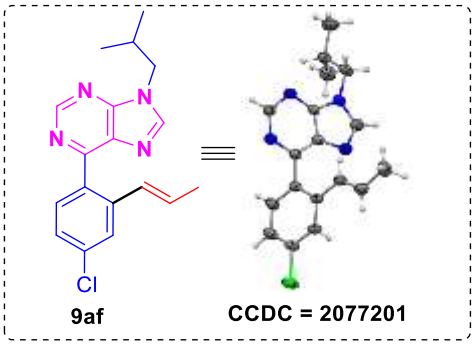
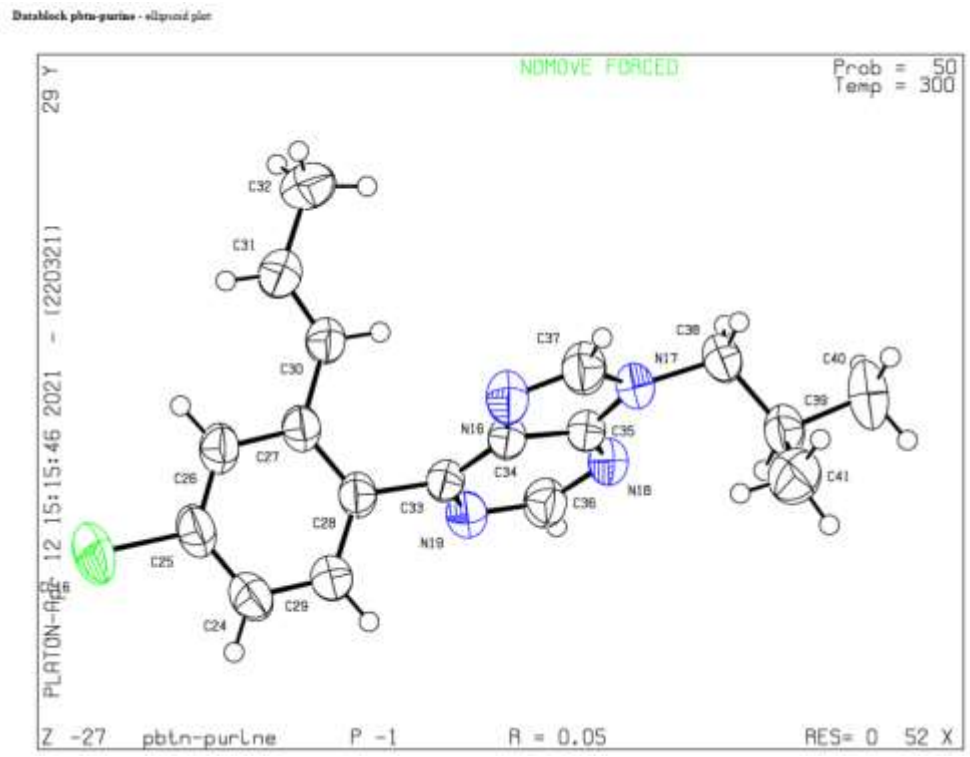


Figure S1. Crystal structure of **9af** (50% ellipsoid probability)

Table S2 Crystal data and structure refinement for PBTN-PURINE.

Identification code	PBTN-PURINE
Empirical formula	$C_{18}H_{18}ClN_4$
Formula weight	325.81
Temperature/K	299.7(5)
Crystal system	triclinic
Space group	P-1
a/Å	9.4208(3)
b/Å	10.0653(3)
c/Å	10.3448(3)
α/°	65.854(3)
β/°	83.509(3)
γ/°	69.754(3)
Volume/Å^3	839.33(5)
Z	2
ρ_{calc}g/cm^3	1.289
μ/mm^{-1}	2.040
F(000)	342.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.374 to 151.084

Index ranges	$-11 \leq h \leq 11, -12 \leq k \leq 12, -12 \leq l \leq 12$
Reflections collected	11437
Independent reflections	3333 [R_{int} = 0.0435, R_{sigma} = 0.0410]
Data/restraints/parameters	3333/0/211
Goodness-of-fit on F^2	1.116
Final R indexes [I>=2σ (I)]	R_1 = 0.0740, wR_2 = 0.1600
Final R indexes [all data]	R_1 = 0.0793, wR_2 = 0.1647
Largest diff. peak/hole / e $Å^{-3}$	0.19/-0.29



(b) Crystals of the compounds **Int-2** were obtained after slow evaporation of MeOH. Crystals suited for single crystal X-Ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with a Rigaku Smartlab X-ray diffractometer equipped with graphite-monochromated (Cu-Kα radiation, λ = 1.54184, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT and SMART software packages and corrected for absorption with SADABS. The structure was solved by direct methods and refined on F2 with SHELXL-97 using Olex-2 software.

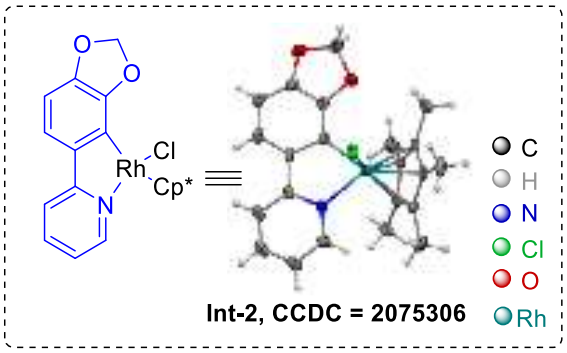


Figure S2. Crystal structure of **Int-2** (50% ellipsoid probability).

Table S3 Crystal data and structure refinement for pcr-pb-tn-1nt-oxobri.

Identification code	pcr-pb-tn-1nt-oxobri
Empirical formula	$C_{22}H_{23}ClNO_2Rh$
Formula weight	471.77
Temperature/K	299.7(3)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.79550(10)
b/Å	7.59350(10)
c/Å	15.85550(10)
α/°	90
β/°	91.3970(10)
γ/°	90
Volume/Å^3	1901.19(3)
Z	1
ρ_{calc}g/cm^3	0.412
μ/mm^{-1}	2.173
F(000)	240.0
Crystal size/mm^3	0.17 × 0.16 × 0.13
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.806 to 148.996
Index ranges	-19 ≤ h ≤ 19, -9 ≤ k ≤ 6, -19 ≤ l ≤ 19
Reflections collected	27928
Independent reflections	3854 [R_{int} = 0.0441, R_{sigma} = 0.0211]
Data/restraints/parameters	3854/0/249
Goodness-of-fit on F^2	1.102
Final R indexes [I>=2σ (I)]	R_1 = 0.0243, wR_2 = 0.0644
Final R indexes [all data]	R_1 = 0.0251, wR_2 = 0.0647
Largest diff. peak/hole / e Å^{-3}	0.31/-0.61

Datablock pcr-pb-tn-1nt-oxobri - ellipsoid plot