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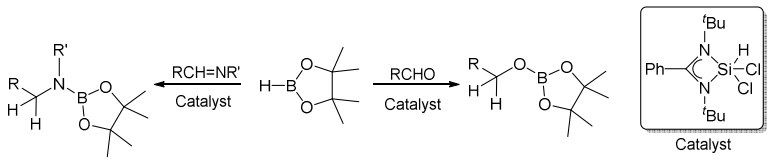
Graphical Abstract

for

Transition metal free catalytic hydroboration of aldehydes and aldimines by amidinato silane

Milan Kumar Bisai,[a] Sanjukta Pahar,[a] Tamal Das,[b] Kumar Vanka*[b] and Sakya S. Sen*[a]



Benz-aimidinato dichlorosilane [PhC(N*t*Bu)$_2$SiHCl$_2$] has been reported to catalyze hydroboration of aldehydes at room temperature and aldimines with slightly forcing conditions.

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Communication

Transition metal free catalytic hydroboration of aldehydes and aldimines by amidinato silane

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The transition metal free catalytic hydroboration of aldehydes and ketones is very limited and has not been reported with a well-defined silicon(IV) compound. Therefore, we chose to evaluate the previously reported silicon(IV) hydride [PhC(N*t*Bu)$_2$SiHCl$_2$], (1) as a single component catalyst and found that it catalyzes the reductive hydroboration of a range of aldehydes with pinacolborane (HBpin) at ambient conditions. In addition, compound 1 can catalyze imine hydroboration. DFT calculation was carried out to understand the mechanism.

The addition of a B-H bond to the C=C, C=O, and C=N bonds requires a catalyst. Group 4 metallocenes[1] and precious metal compounds, especially organometallic rhodium and iridium complexes[2] are the most studied catalysts for hydroboration reactions. Due to the environmental concern, limited terrestrial abundance, the high cost of traditional transition metal catalysts, there is a recent surge to explore compounds with main group elements as feasible alternatives of transition metal catalysts.[3-6] Encouragingly, a number of research groups such as Hill, Roesky, Wesemann, Nembenna, Jones, Zhao, Kinjo, and others[7-13] have started to use compounds with *s*- and *p*-block elements as single site catalysts for catalytic hydroboration of aldehydes and ketones (Scheme 1). However, when we look at the full gamut of single site neutral compounds reported for transition metal free hydroboration of aldehydes and ketones, there is one element missing that one might have expected to be there: silicon.

Being an isostere of carbon and owing to the larger covalent radius, electropositive nature, low toxicity and relative abundance, silicon compounds are highly sought after as single component catalysts because a catalytic cycle based on silicon could be sustainable, economical and green. Silylium ions promoted catalytic imine reduction and Diels–Alder reactions[14a,b,g] and bis(perfluorocatecholato)silane [Si(cat^F)$_2$] catalyzed aldehyde hydrosilylation[14c] have been lately reported illustrating the potential of silicon compounds as catalysts. Besides, there are recent theoretical and experimental reports on formylation of amines using a comibation of CO_2 and a silane as the formylation reagent.[14d-e] Cantat et al. very recently reported the hydroboration of CO_2 using an well-defined guanidine substituted hydrosilane.[14f] Boosted by the success of alanes (**A**-**C**) and phosphane (**G**), we were interested in exploring the catalytic potential of previously reported benz-amidinato silane [PhC(N*t*Bu)$_2$SiHCl$_2$], (**1**),[15a] for hydroboration reaction. Our results are reported herein.

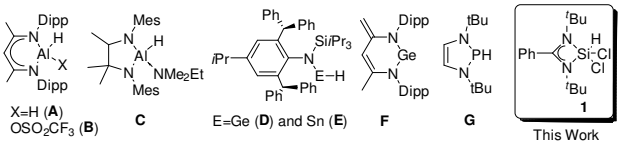
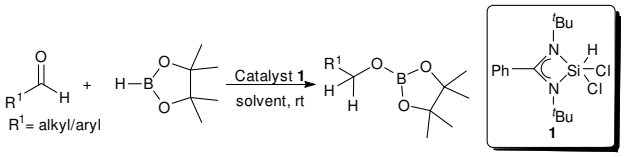


Chart 1. Single component compounds with heavier p-block elements that catalyzes hydroboration of aldehydes (**A**-**G**); This work reports the first use of a neutral silicon (IV) compound (**1**) for aldehyde hydroboration.



Scheme 1. Silicon(IV) hydride (**1**) catalyzed hydroboration of aldehydes.

Compound **1** was previously reported by Roesky et al. as a precursor for silicon(II) chloride[15a] and silicon(II) bis(trimethylsilyl)amide.[15b] Compound **1** was chosen as a catalyst for hydroboration reaction because it can be synthesized in a single step with high yield.[15a] Direct addition of HBpin to benzaldehyde in absence of the catalyst only afforded trace amount of $PhCH_2OBpin$; an observation also noted by others.[7,8,11,12] However, when the reaction was

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This paper is dedicated to Professor Didier Astruc on the occasion of his 70th birthday
Electronic Supplementary Information (ESI) available: Experimental Details, characterization data and details of computational methodology are given in the supporting information.

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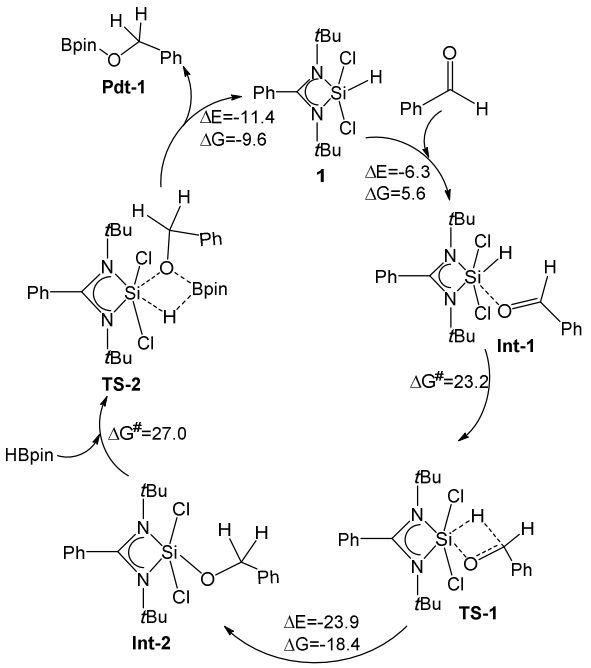
carried out in presence of 1 mol% of **1**, it led to the quantitative conversion to $PhCH_2OBpin$ at room temperature in an hour (Scheme 2). When the catalyst loading was reduced to 0.5 mol%, the conversion was still achieved albeit with slightly lower yield (77%) (See Supporting Information, Table S1). Therefore, each reaction was conducted at room temperature with 1 mol% catalyst in an equimolar mixture of aldehyde and HBpin. We have also performed the reaction in presence of only 1 mol% of $HSiCl_3$ as a catalyst, but only trace amount of product formation was observed. We have explored the reactions in various solvents such as benzene, toluene, dichloroethane and observed that the identity of the solvent had little effect on the yields. The products were identified by a combination of GC-MS, ^1H and ^{13}C NMR spectroscopies.

In order to understand possible mechanistic pathway, simple NMR experiments were performed. As silicon is in +4 oxidation state, it is expected that the catalysis will occur via σ-bond metathesis, which has a modicum of precedence for non-metal p-block elements.[16] When a 1:1 mixture of **1** and benzaldehyde in $CDCl_3$ was monitored by ^1H NMR, the development of a new singlet at δ 5.05 ppm was observed with concomitant disappearance of the aldehyde proton (δ 9.95 ppm) as well as Si-H proton (δ 6.26 ppm).[15a] The ^{13}C NMR spectrum was (in $CDCl_3$) also changed, with a new peak appearing at δ 66.00 ppm for [-O*C*H_2-] substituent, which was further confirmed by DEPT experiments. The ^{29}Si NMR spectrum showed a new resonance at δ –101.2 ppm, which is slightly upfield shifted than that in **1** (δ –96.6 ppm) but in good agreement with the previously reported penta-coordinate silicon compounds bearing a Si–O bond such as $[PhC(NtBu)_2SiCl_2OR$, (R=*i*Pr and *t*Bu)].[15c] Taken together, these data suggest the possible formation of alkoxy compound $[PhC(NtBu)_2SiCl_2OCH_2Ph]$ (**Int-2**) as an intermediate. However, even after repeated attempts, we could not obtain the single crystals of **Int-2**. In order to prove the formation of **Int-2** during the catalytic cycle, we performed the metathetical reaction between $[PhC(NtBu)_2SiCl_3]$[17] and potassium benzyloxide, which also led to **Int-2**. Comparison of spectra obtained from two different reactions unequivocally confirms that **Int-2** was being formed during the catalytic cycle. The formation of a strong Si–O bond can be presumed as the driving force for the metathesis reaction.[18]

Full quantum mechanical calculations were done with density functional theory (DFT) at the dispersion and solvent corrected PBE/TZVP level of theory in order to understand the mechanism (Figure S1 and Scheme 2) of the aldehyde hydroboration reaction in the presence of the catalyst **1** [for further details, please see the Supporting Information]. In the first step of the reaction, a loosely bound complex (**Int-1**) is formed between the catalyst **1** and benzaldehyde, with the benzaldehyde approaching towards the catalyst from the direction opposite to the Si–N bond. The reaction energy (ΔE) and the Gibbs free energy (ΔG) for this step are –6.3 kcal/mol and 5.6 kcal/mol, respectively. This is the prelude to the nucleophilic attack by the carbonyl oxygen of benzaldehyde to the silicon centre of the catalyst, with the hydride being transferred from the silicon centre to the electrophilic carbonyl carbon of the benzaldehyde. This occurs through a four-membered transition state (**TS-1**) and leads to the formation of **Int-2** (see Figure 1). The ΔE (-23.9 kcal/mol) and ΔG (-18.4 kcal/mol) values for this step are highly negative and the activation energy ($\Delta G^{\#}$) barrier corresponding to the transition state is 28.8 kcal/mol, which is moderate and explains why the reaction can take place at room temperature. This is also the slowest step of the overall hydroboration reaction. The silicon centre of catalyst **1** therefore acts as the hydride donor to the electrophilic carbonyl carbon centre.



Scheme 2. The catalytic cycle and reaction mechanism for the benzaldehyde hydroboration by catalyst **1**, calculated at the PBE/TZVP level of theory with DFT.ΔG and $\Delta G^{\#}$ represent the Gibbs free energy of reaction and the Gibbs free energy of activation respectively. All values are in kcal/mol.

In the next step, pinacolborane approaches the Si-O bond of **Int-2**, which then passes through a Si-O-B-H four membered cyclic transition state (**TS-2**), leading to the formation of the hydroboration product (**Pdt-1**) along with the regeneration of the catalyst. The regeneration of the catalyst has also been observed in the ^1H NMR spectroscopy from the stoichiometric reaction between **Int-2** and HBpin with the reappearance of the Si-H resonance at δ 6.26 ppm in the reaction mixture with concomitant disappearance of the B-H protons. The four-membered cyclic transition state (**TS-2**) involves a H-bonding interaction between the Si and B atoms and in this transition state there is a significant amount of B-H bond activation takes place (1.27 Å) in comparison to that in HBpin (1.19 Å). Such elongation allows the hydride transfer from the boron to the silicon atom leading to the simultaneous Si-O bond cleavage and B-O bond formation. Similar mechanistic proposal for the regeneration of aluminum hydride catalyst was suggested by

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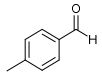
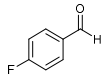
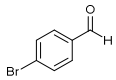
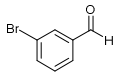
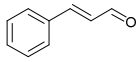
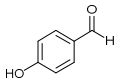
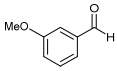
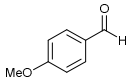
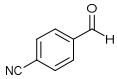
Zhi, Parameswaran, and Roesky. The driving force of the reaction can be attributed to the oxophilicity of the boron atom.[19] The ΔE (-11.4 kcal/mol) and ΔG (-9.6 kcal/mol) values for this step are highly negative and the barrier ($\Delta G^{\#}$) is 27.1 kcal/mol. To confirm the slowest step, we have employed the energetic span model (ESM) calculations[20] and have found that the percentage contribution for the 1st and 2nd transition states are 95% and 5%. Hence the first step is seen to be the slowest step of the overall hydroboration process.

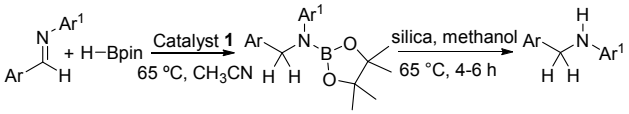
Table 1. Hydroboration of aldehydes catalyzed by 1.[a]

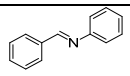
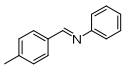
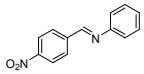
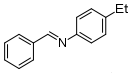
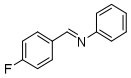
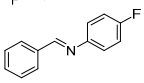
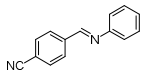
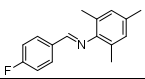
Entry	Substrate	Cat (mol%)	Time [h]	Yield [%][b]
1		-	0.5	trace
2		1	1	96
3		1	1	90
4		1	1	90
5		1	1	88
6		1	1	85
7		1	1	82
8		1	1.5	95
9		1	1	75
10		1	1	72
11		1	1	84
12		1	1	70
13		1	1	90
14		1	1	52
15		1	5	95

[a]All reactions carried out in benzene at room temperature using 1 equiv of HBpin. [b]Conversion was determined by NMR spectroscopy on the basis of the consumption of the aldehyde and the identity of the product was confirmed by RCH_2OBpin or resonances.

Subsequently, the scope of the catalytic reaction was examined with a range of aldehydes. Reactions were monitored by ^1H NMR spectroscopy with the appearance of new upfield resonances corresponding to the α-protons of the boronate ester. Most of the aromatic aldehydes are converted to the corresponding boronate esters at room temperature in short reaction time in good yields (entries 1-15). No inhibitory effect was observed for *ortho* substituents (entries 7 and 9). The reaction showed tolerance towards fluoride groups, as demonstrated by the clean hydroboration of 4-fluorobenzalhedye (entry 4). When salicylaldehyde or 4-hydroxybenzaldehyde were used, hydroboration was occurred at the aldehyde functional group as well as double hydroboration was occurred in aldehyde and OH groups (minor products) (entries 9 and 10). However, only hydroxylborane dehydrocoupled product has not been formed. Hydroboration of cinnamaldehyde led to the 1,2-adducts, keeping the olefinic functionality intact (entry 8). The reaction of 4-pyridine-carboxaldehyde with HBpin led to exclusive hydroboration of the carbonyl functionality instead of pyridine dearomatization (entry 13).

Table 2. Hydroboration of imines Catalyzed by **1** and the conversion of amine boronates to secondary amines.[a]



Entry	Substrate	Cat (mol%)	Time [h]	Yield [%][b]
1		2	48	86
2		2	48	74
3		2	48	87
4		2	50	88
5		2	72	76
6		2	72	79
7		2	72	88
8		2	72	52

[a]All reactions carried out in acetonitrile at 65 °C using 1 equiv of HBpin. [b]Yields are isolated yield of secondary amines.

We further examined the scope of hydroboration for ketones. However, even after increasing the mol% of the

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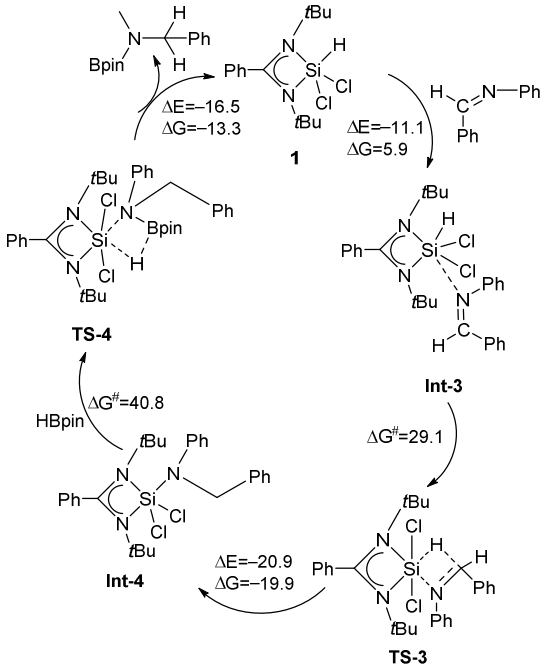
catalyst, reaction temperature, time, changing solvent did not lead to the hydroboration of ketone. In fact, no reaction was observed between **1** and ketone which can be attributed to the higher coordination and sterics around the silicon atom. Consistent with that, theoretical calculations also reveal that both barriers are substantially higher for ketones than those of aldehydes.

The silane catalyzed hydroboration has been extended to imines; which has been scarcely studied. The first transition metal-catalyzed imine hydroboration was reported by Baker and Westcott et al. using Au complexes,[21] which were followed by few more reports.[22-25] The transition metal free imine hydroboration was reported by the group of Hill using magnesium compound [CH{C(Me)NAr}$_2$Mg*n*Bu] (Ar=2,6-*i*Pr$_2$C$_6$H$_3$)[26] and the group of Crudden using Lewis adduct of DABCO and B(C$_6$F$_5$)$_3$.[27] It was observed that **1** catalyzes hydroboration of imines with slightly harsher condition. Purification of products by SiO_2 column chromatography led exclusively to corresponding secondary amines.



Scheme 3. The catalytic cycle and reaction mechanism for the imine hydroboration by catalyst **1**, calculated at the PBE/TZVP level of theory with DFT. ΔG and ΔG$^{\#}$ represent the Gibbs free energy of reaction and the Gibbs free energy of activation respectively. All values are in kcal/mol.

We have also carried out quantum mechanical calculations to explore the reaction mechanism at the same level of theory for the imine hydroboration in the presence of the silane catalyst (Scheme 3 and Figure S1). The bond making and breaking between the Si–N and B–H bond are involved in the transition state (**TS-4**) with a significant B–H bond activation (1.28 Å). The only differences in this case compared to those of aldehydes are the energy barriers, especially at the second transition state (**TS-4**), with the barrier being 40.8 kcal/mol. This higher barrier explains why the reaction requires heating to 65 °C.

In summary, we have demonstrated the first use of a well-defined neutral silicon(IV) compound for catalytic hydroboration of aldehydes and aldimines. The initial step in the catalytic cycle is the facile addition of the Si–H bond to the C=O bond via a four-membered transition state. The second step involves the σ-bond metathesis between [PhC(N*t*Bu)$_2$SiCl$_2$OCH$_2$Ph] (**Int-2**) and HBpin resulting in the product formation along with the regeneration of the catalyst. The mechanism was further supported by DFT calculations. We believe that our findings will spur more interest among researchers to design many more silicon(IV) compounds as catalysts for various organic transformations.

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Supplementary Information

for

Transition metal free catalytic hydroboration of aldehydes and aldimines by amidinato silane

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General Experimental Information

All reactions were performed under argon atmosphere using Schlenk techniques or inside aM Braun glove box. Pinacolborane (HBpin), aldehydes were purchased from Sigma–Aldrich, Alfa–Aesar, and TCI and used without further purification. Imines obtained from benzaldehyde derivatives were prepared by stirring the carbonyl precursor with 1.1 equivalents of the relevant amine in dichloromethane over molecular sieves for 18 hours at room temperature, followed by filtration, solvent removal and recrystallization of the imine from hexanes.[S1] Compound **1** was synthesized by a literature procedure.[S2] Benzene was distilled from Na/benzophenone and further dried by molecular sieves prior to use. Acetonitrile was used from MBraun-SPS 800. C_6D_6 and $CDCl_3$ were purchased from Sigma-Aldrich, were degassed by three freeze-pump-thaw cycles, and stored over molecular sieves. ^1H, $^{13}C\{^1H\}$NMR spectra were recorded on Bruker AV–200MHz and referenced to the resonances of the solvent used.

Stoichiometric reaction of catalyst 1 and benzaldehyde

A solution of Benzaldehyde (0.1 g, 1 mmol) in toluene (5 mL) was added dropwise to the toluene solution (15 mL) of **1** (0.3 g, 1 mmol) at –60 °C. The reaction mixture was stirred at room temperature overnight. Volatiles of the mixture were removed under reduced pressure. The residue was extracted with toluene and concentration of the solution led to colorless solid of **Int-2**. Yield **(**0.40 g, 49%**)**,^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 7.80-7.28 (m, 10H, Ar*H*), 5.05 (s, 2H, OCH_2), 1.17 (s, 18H, CH_3) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$, 125.70 MHz, 298 K): δ 31.56 (*C*H_3), 55.45 (*C*$(CH_3)_3$), 66.00 (O*C*H_2), 155.15 (N*C*N) ppm; $^{29}Si\{^1H\}$NMR ($CDCl_3$, 500 MHz, 298 K): δ -101.28 ppm.

*Note: The formation of **Int-2** was always accompanied with the formation of free amidinate ligand! As a result designation of phenyl carbons in **Int-2** from the ^{13}C NMR spectrum was difficult.*

Alternative Preparation of Int-2. To the solution of KOBn (0.2 g, 1.36 mmol) in 10 mL toluene, toluene solution (20 mL) of PhC(N*t*Bu)$_2$SiCl$_3$ (0.5 g, 1.36 mmol) was added drop by drop at -78 ^{o}C. The reaction mixture was stirred for 30 min at -78 ^{o}C and then slowly allowed to room temperature and stirred overnight. The filtrate was collected by filtration through celite pad glass frit, concentrated under vacuum and kept for crystallization. Yield: 52%.

General catalytic procedure for the hydroboration of aldehydes

Aldehyde (0.5 mmol), pinacolborane (0.5 mmol), catalyst (1 mol%), benzene (1 mL) were charged in a Schlenk tube with a magnetic bead inside the glove box. The reaction mixture was allowed to stir at room temperature. The progress of the reaction was monitored by ^1H

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NMR, which indicated the completion of the reaction by the disappearance of aldehyde (RC*H*O) proton and appearance of a new OCH_2 resonance. For isolation of corresponding primary alcohol of few aldehyde, reactions were scaled up and carried out at same reaction condition as mentioned.

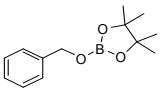
Upon completion of the reaction, three of the resulted boronate ester residue were hydrolysed by silica gel with methanol at 60 °C for 4–6 hrs. The completion of hydrolysis was checked by TLC. Upon completion, the reaction mixture was filtered and washed three times with dichloromethane. The combined organic layers were dried, evaporated and the residue was purified by column chromatography over silica gel (100–200 mesh) with pet ether/ethyl acetate (20:1) mixture as eluent, which provided the pure primary alcohols.

Table S1. Optimization Table of Hydroboration of Benzaldehyde Catalysed by 1 in benzene

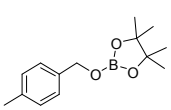
entry	catalyst (mol%)	temp.	Time (h)	Conv. (%)
1	**0.5**	**rt**	**1**	**77**
2	**0.5**	**50 °C**	**1**	**88**
3	**1.0**	**rt**	**1**	**96**
4	**1.5**	**rt**	**1**	**96**

Analytical data and NMR (^{1}H, ^{13}C) spectra of boronate esters of corresponding aldehydes

2-(benzyloxy)-pinacolborane (2): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.28-7.18 (m, 5H, Ar*H*), 4.85 (s, 2H, OCH_2), 1.18 (s, 12H, CH_3) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.48 (*C*H_3), 66.55 (*C*H_2), 82.90 (*C*$(CH_3)_2$), 126.65 (*Ph*), 127.27 (*Ph*), 128.20 (*Ph*), 139.16 (Ar*C*-R) ppm.



2-((4-methylbenzyl)oxy)-pinacolborane (3): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.18-7.14 (d, $^3J_{H-H}$=8.0 Hz, 2H, Ar*H*), 7.07-7.03 (d, $^3J_{H-H}$=7.9Hz, 2H, Ar*H*), 4.80 (s, 2H, CH_2), 2.25 (s, 3H, ArCH_3), 1.18 (s, 12H, CH_3) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 21.05 (Ar-*C*H_3), 24.54(*C*H_3), 66.51(*C*H_2), 82.80 (*C*$(CH_3)_2$), 126.77 (*Ph*), 126.87 (*Ph*), 136.19 (*Ph*), 139.90 (*Ph*) ppm.



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2-((4-fluorobenzyl)oxy)-pinacolborane (4): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.30-6.85 (m, 4H, Ar*H*), 4.80 (s, 2H, CH_2), 1.19 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.51 (*C*H_3), 65.98 (*C*H_2), 83.01 (*C*$(CH_3)_2$), 115.05 (d, $J_{C\text{-}F}$=21.22 Hz, Ar-*C*), 128.58 (d, J_{C-F}=8.05 Hz, Ar-*C*), 134.88 (Ar-C), 162.13 (*d*, $J_{C\text{-}F}$ = 245.17 Hz, Ar*C*-F) ppm.

2-((4-bromobenzyl)oxy)-pinacolborane (5): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.36 (d, 2H, Ar*H*), 7.12(d, 2H, Ar*H*), 4.78 (s, 2H, CH_2), 1.18 (s, 12H, CH_3) ppm.

2-((3-bromobenzyl)oxy)-pinacolborane (6): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.49-7.06 (m, 4H, Ar*H*), 4.81 (s, 2H, CH_2), 1.19 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.56 (*C*H_3), 65.77 (*C*H_2), 83.12 (*C*$(CH_3)_2$), 125.09 (*Ph*), 129.66 (*Ph*), 129.81 (*Ph*), 130.37 (*Ph*), 137.24 (*Ph*), 141.45 (*Ph*) ppm.

2-((2-bromobenzyl)oxy)-pinacolborane (7): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.47-6.97(m, 4H, Ar*H*), 4.90(s, 2H, CH_2), 1.19 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.53 (*C*H_3), 66.21 (*C*H_2), 83.08 (*C*$(CH_3)_2$), 121.45 (*Ph*), 127.27 (*Ph*), 127.73 (*Ph*), 128.54 (*Ph*), 132.18 (*Ph*),138.25 (*Ph*) ppm.

2-(cinnamyloxy)-pinacolborane (8): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.32-7.09 (m, 5H, Ar*H*), 6.61-6.49 (d, 1H, $^{3}J_{H\text{-}H}$=15.7 Hz, 1H ArC*H*), 6.29-6.13 (m, 1H, CHC*H*), 4.48-4.45 (d, 2H, $^{3}J_{H\text{-}H}$=5.3 Hz, CH_2), 1.18 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.51 (*C*H_3), 65.17 (*C*H_2), 82.87 (*C*$(CH_3)_2$), 126.34 (*Ph*), 126.69 (*Ph*), 127.42 (*Ph*), 128.43 (Ar-*C*H), 130.54 (Ar-CH*C*H), 136.76 (Ar*C*-R) ppm.

2-(2-hydroxybenzyloxy)-pinacolborane (9): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.11-7.07 (d, $^{3}J_{H\text{-}H}$=7.58 Hz, 2H, Ar*H*,), 6.84-6.79 (m, 2H, Ar*H*), 4.90 (s, 2H, CH_2), 1.19 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.45 (*C*H_3), 64.50 (*C*H_2), 83.49 (*C*$(CH_3)_2$), 116.85 (*Ph*), 124.11 (*Ph*), 128.23 (*Ph*), 129.22 (*Ph*), 129.49 (*Ph*), 152.02 (Ar*C*-OH) ppm.

2-(4-hydroxybenzyloxy)-pinacolborane (10): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.19-6.90 (m, 4H, Ar*H*), 4.76 (s, 2H, CH_2), 1.18 (s, 12H, CH_3) ppm; ^{13}C NMR

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($CDCl_3$, 50.28 MHz, 298 K): δ 24.41 (*C*H_3), 66.55 (*C*H_2), 83.04 (*C*$(CH_3)_2$), 116.08 (*Ph*), 124.11 (*Ph*), 128.19 (*Ph*),132.45 (*Ph*), 155.59 (Ar*C*-OH) ppm.

2-((3-methoxybenzyl)oxy)-pinacolborane (11): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.20-6.67 (m, 4H, Ar*H*), 4.83 (s, 2H, CH_2), 3.71 (s, 3H, OCH_3), 1.18 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.49 (*C*H_3), 55.05 (O*C*H_3), 66.43 (*C*H_2), 82.89 (*C*$(CH_3)_2$), 111.74 (*Ph*), 113.07 (*Ph*), 118.77 (*Ph*), 129.20 (*Ph*), 140.73 (*Ph*), 159.57 (Ar*C*-OMe) ppm.

2-((4-methoxybenzyl)oxy)-pinacolborane (12): ^{1}HNMR ($CDCl_3$, 200 MHz, 298 K): δ 7.22-7.17 (d, $^3J_{H\text{-}H}$=8.84 Hz, 2H, Ar*H*), 6.80-6.76 (d, $^3J_{H\text{-}H}$=8.72 Hz, 2H, Ar*H*), 4.77 (s, 2H, CH_2), 3.70 (s, 3H, OCH_3), 1.18 (s, 12H, CH_3) ppm.

4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)pyridine (13): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 8.51-8.48 (d, $^3J_{H\text{-}H}$=6.06 Hz, 2H, Ar*H*), 7.21-7.18 (d, $^3J_{H\text{-}H}$=5.81 Hz, 2H, Ar*H*), 4.87 (s, 2H, CH_2), 1.19 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.48 (*C*H_3), 64.86 (*C*H_2), 83.21 (*C*$(CH_3)_2$), 120.79 (*Ph*), 128.20 (*Ph*), 149.36 (*Ph*) ppm.

4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzonitrile (14): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.56-7.52(d, $^3J_{H\text{-}H}$=8.46 Hz, 2H, Ar*H*), 7.38-7.33(d, $^3J_{H\text{-}H}$=7.83 Hz, 2H, Ar*H*), 4.89 (s, 2H, CH_2), 1.19 (s,12H, CH_3) ppm.

2-isobutoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 3.60 (d, $^3J_{H\text{-}H}$=6.57 Hz, 2H, CH_2), 1.81 (sept, 1H, C*H*$(CH_3)_2$) , 1.25 (s, 12H, CH_3), 0.88 (d, $^3J_{H\text{-}H}$=6.69 Hz, 6H, CH(CH_3)$_2$) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 82.42 (*C*$(CH_3)_2$),, 71.21 (*C*H_2), 29.68 (*C*H$(CH_3)_2$, 24.43 (*C*H_3), 18.61 (*C*H_3) ppm.

Isolation of primary alcohols

In three cases, we have performed the hydrolysis and isolated the primary alcohols:

4-bromo benzyl alcohol (5'): Yield: 146.5 mg (78.3%); ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.42-7.37 (d, $^3J_{H\text{-}H}$=8.46 Hz, 2H, Ar*H*), 7.17-7.13 (d, ^3J=7.83 Hz, 2H, Ar*H*), 4.55 (s, 2H, CH_2), 1.61 (s, 1H, O*H*) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 64.58 (CH_2), 128.32 (*Ph*), 128.57 (*Ph*), 139.74 (*Ph*) ppm.

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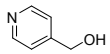
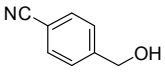
(Pyridine-4-yl)methanol (13'): Yield: 89.5 mg (83%); ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K):



δ 8.48-8.45 (d, $^{3}J_{H\text{-}H}$=5.94 Hz, 2H, Ar*H*), 7.31-7.28 (d, $^{3}J_{H\text{-}H}$=6.06 Hz, 2H, Ar*H*), 4.74 (s, 2H, CH_2), 3.99 (s, 1H, O*H*) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 62.97 (*C*H_2), 121.20(*Ph*), 149.27(*Ph*), 151.02 (*Ph*) ppm.

4-cyano benzylalcohol (14'): Yield: 53 mg (40%); ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.67-7.63 (d, $^{3}J_{H\text{-}H}$=8.34 Hz, 2H, Ar*H*), 7.50-7.46 (d, $^{3}J_{H\text{-}H}$=8.59 Hz, 2H, Ar*H*), 4.79 (s, 2H, CH_2), 2.05 (s, 1H, O*H*) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.7 (*C*H_3), 64.17 (*C*H_2), 111.11 (*C*-CN), 118.83 (*C*N), 126.98 (*Ph*), 132.28 (*Ph*), 146.19 (Ar*C*-CN) ppm.



General catalytic procedure for the hydroboration of Imines

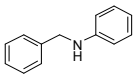
Imine (1 mmol), pinacolborane (1 mmol), catalyst **1**(2 mol %), acetonitrile (1 mL) were charged in a Schlenk tube with a magnetic bead inside the glove box. The reaction mixture was allowed to stir at room temperature and then slowly heated at 65 ^{o}C for 48-72 h. The progress of the reaction was monitored by ^{1}H NMR, which indicated the completion of the reaction by the disappearance of Imine (RC*H*NR´) proton and appearance of a new CH_2 resonance. Upon completion of the reaction, resulted boronate ester residues were hydrolysed with silica gel and methanol at 65 °C for 4-6 h. The completion of hydrolysis was checked by TLC. Upon completion, the reaction mixture was filtered and washed three times with dichloromethane. The combined organic layers were dried, evaporated and the residue was purified by column chromatography over silica gel (100–200 mesh) with pet ether/ethyl acetate (1:5) mixture as eluent, which provided the pure secondary amines.

Table S2. Optimization Table of Hydroboration of diphenyl imines Catalysed by 1 in acetonitrile

entry	catalyst (mol%)	temp.	Time (h)	Conv. (%)
1	1	rt	24	0
2	2	rt	24	Trace
3	2	65^{o}C	24	70
4	2	65^{o}C	48	95

Isolation of secondary amines

N-benzylaniline (16): Isolated Yield: 157.5 mg (86%); ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K):



δ 7.36-7.13 (m, 7H, Ar*H*), 6.74-6.61 (m, 3H, Ar*H*), 4.32 (s, 2H, CH_2), 4.01 (s, 1H, N*H*) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 148.11, 139.40,

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129.23, 128.60, 127.48, 127.19, 117.53, 112.81 (*Ph*), 48.29 (*C*H_2) ppm.

N-(4-methylbenzyl)aniline (17): Isolated Yield: 146 mg (74%); ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.20-7.05 (m, 6H, Ar*H*), 6.67-6.53 (m, 3H, Ar*H*), 4.20 (s, 2H, CH_2), 3.89 (s, 1H, N*H*), 2.26 (s, 3H, CH_3) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 148.19, 136.84, 136.33, 129.27, 129.22, 127.49, 117.45, 112.80 (*Ph*), 48.05 (*C*H_2), 21.07 (*C*H_3) ppm.

N-(4-nitrobenzyl)aniline (18): Isolated Yield: 198.5 mg (87%); ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 8.20-8.16 (d, $^3J_{H-H}$ =8.84 Hz, 2H, Ar*H*), 7.55-7.51 (d, $^3J_{H-H}$ =8.84 Hz, 2H, Ar*H*), 7.22-7.12 (m, 2H, Ar*H*), 6.78-6.71 (t, $^3J_{H-H}$ =7.0 Hz,1H, Ar*H*), 6.60-6.56 (d, $^3J_{H-H}$ =7.58 Hz, 2H, Ar*H*), 4.47 (s, 2H, CH_2), 4.25 (s, 1H, N*H*) ppm;^{13}C{^{1}H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 147.47, 147.29, 147.15, 129.35, 127.66, 123.85, 118.18, 112.88 (*Ph*), 47.58 (*C*H_2) ppm.

N-benzyl-4-ethylaniline (19): Isolated Yield: 186 mg (88%); ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.31-7.11 (m, 5H, Ar*H*), 6.95-6.90 (d, $^3J_{H-H}$ =8.46 Hz, 2H,Ar*H*), 6.51-6.47 (d, $^3J_{H-H}$ =6.46 Hz, 2H, Ar*H*), 4.21 (s, 2H, CH_2), 3.81 (s, 1H,N*H*), 2.51-2.39 (q, $^3J_{H-H}$ =22.74 Hz, 2H, CH_2CH$_3$),1.14-1.06 (t, $^3J_{H-H}$ =15.16 Hz, 3H, CH_2CH_3) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 146.06, 139.61, 133.43, 128.55, 127.51, 127.13, 112.98 (*Ph*), 48.65 (*C*H_2NH), 27.90 (*C*H_2CH$_3$), 15.92 (CH_2*C*H_3) ppm.

N-(4-fluorobenzyl)aniline (20): Isolated Yield: 152.9 mg (76%); ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.28-7.21 (m, 2H, Ar*H*), 7.15-7.05 (m, 2H, Ar*H*), 6.98-6.89 (m, 2H, Ar*H*), 6.68-6.51 (m, 3H, Ar*H*), 4.21 (s, 2H, CH_2), 3.92 (s, 1H, N*H*) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 162.01 (d, J_{C-F}=245.17 Hz, Ar*C*-F), 147.90 (*Ph*), 135.10 (*Ph*), 129.25 (*Ph*), 128.96 (d, J_{C-F}=8.05 Hz, *Ph*), 117.71, (*Ph*), 115.40 (d, J_{C-F}=21.22 Hz, Ar-*C*), 112.85 (*Ph*), 47.57 (*C*H_2) ppm.

N-benzyl-4-fluoroaniline (21): Isolated Yield: 158.9 mg (79%); ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.36-7.23 (m, 5H, Ar*H*), 6.91-6.82 (m, 2H, Ar*H*), 6.58-6.51 (m, 2H, Ar*H*), 4.27 (s, 2H, CH_2), 3.92 (s, 1H, N*H*) ppm; ^{13}C{1H} NMR ($CDCl_3$,

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50.28 MHz, 298 K): δ 155.85 (d, $J_{C\text{-}F}$=234.92 Hz, Ar*C*-F), 144.44 (*Ph*), 139.21 (*Ph*), 128.63 (*Ph*), 127.45 (*Ph*), 127.27 (*Ph*), 115.62 (d, $J_{C\text{-}F}$=22.32 Hz, *Ph*), 113.61 (d, J_{C-F}=7.32 Hz, *Ph*), 48.89 (CH_2) ppm.

4-((phenylamino)methyl)benzonitrile (22): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.55-7.51 (d, $^3J_{H\text{-}H}$ =8.46 Hz, 2H, Ar*H*), 7.41-7.37 (d, $^3J_{H\text{-}H}$ =8.08 Hz, 2H, Ar*H*), 7.17-7.05 (q, $^3J_{H\text{-}H}$=6.46 Hz, 2H, Ar*H*), 6.69-6.62 (t, $^3J_{H\text{-}H}$ =14.65 Hz, 1H, Ar*H*), 6.52-6.47 (d, $^3J_{H\text{-}H}$ =7.71 Hz, 2H, Ar*H*), 4.34 (s, 2H, CH_2), 4.14 (s, 1H, N*H*) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 147.35, 145.35, 132.37, 129.30, 127.64, 118.83, 118.03, 112.82, 110.83 (*Ph*), 47.71 (CH_2) ppm.

N-(4-fluorobenzyl)-2,4,6-trimethylaniline (23): Isolated Yield: 126.5 mg (52%); ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.29-7.18 (m, 2H, Ar*H*), 6.99-6.90 (m, 2H, Ar*H*), 6.76 (s, 2H, CH_2), 3.94 (s, 2H, N*H*), 2.95 (s, 1H, CH_3) ppm.

Details of the theoretical calculations

All the calculations in this study have been performed with density functional theory (DFT), with the aid of the Turbomole 6.4 suite of programs,[S3] using the PBE functional.[S4] The TZVP[S5] basis set has been employed. The resolution of identity (RI),[S6] along with the multiple accelerated resolution of identity (marij)[S7] approximations have been employed for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. Dispersion correction (disp3) and solvent correction were incorporated with optimization calculations using the COSMO model,[S8] with dichloroethane (ε = 10.36) as the solvent. The values reported are ΔG values, with zero point energy corrections, internal energy and entropic contributions included through frequency calculations on the optimized minima with the temperature taken to be 298.15 K. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition state structures. The efficiency of a catalytic cycle, as well as the relative prominence of transition states, can be estimated using the *AUTOF* program, which is based on the energetic span model (ESM) defined by Shaik and co-workers.[S9-S11] According to this model, the TOF-determining transition state (TDTS) and intermediate (TDI) can be located from a catalytic cycle by the

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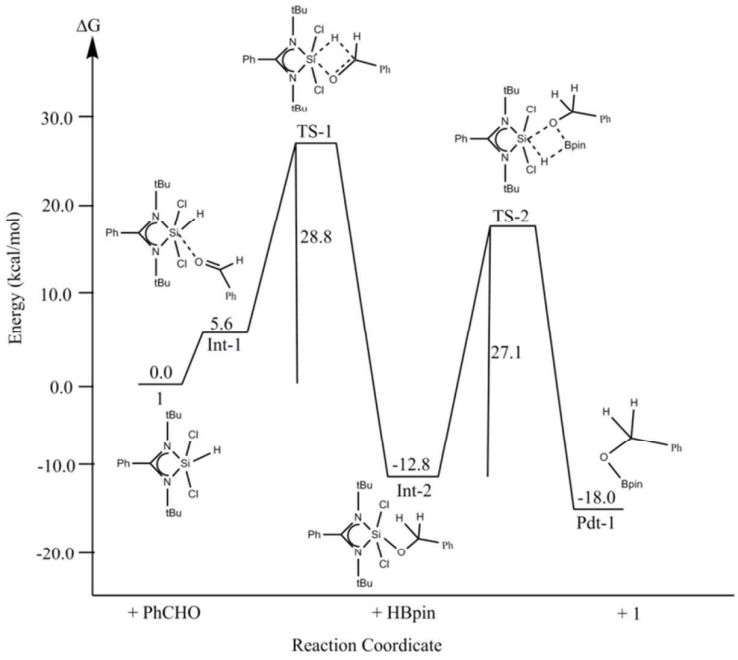
evaluation of the degree of TOF control (X_{TOF}).[56] TOF can be calculated by the following equation:

$$\mathrm{TOF} = \frac{K_B T}{h} \mathrm{e}^{-\delta E / RT}$$

Were δE, the energetic span, can be defined as,

$\delta E = T_{TDTS} - T_{TDI}$ If TDTS appears after TDI

$\delta E = T_{TDTS} - T_{TDI} + \Delta G_r$ If TDTS appears before TDI



Scheme S1. The reaction energy profile diagram for the catalytic hydroboration of benzaldehyde by catalyst **1**. The values (in kcal/mol) have been calculated at the PBE/TZVP level of theory with DFT.

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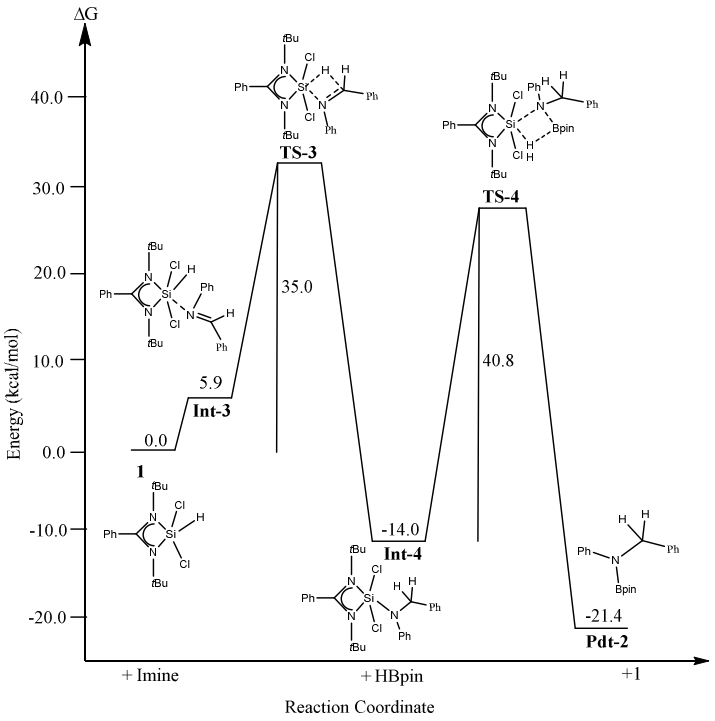

Figure S1. The reaction energy profile diagram for the catalytic imine hydroboration by catalyst **1**. The values (in kcal/mol) have been calculated at the PBE/TZVP level of theory with DFT.

PBE/TZVP optimized geometries for all the compounds and transition states

1

PBE/TZVP Energy : -1195016.22 kcal/mol

Si	8.313878	2.355217	10.541270
Cl	9.678086	0.609181	10.836864
N	7.035584	3.852221	10.650120
C	5.976721	4.430128	9.786181
C	5.927036	3.578702	8.504227
N	8.234040	3.023985	12.260302
C	9.108244	2.930570	13.476744
C	10.572745	3.098504	13.026721
C	7.232577	3.911243	11.954918
C	6.431431	4.693817	12.928371
C	5.515114	4.021819	13.752427
C	4.706960	4.746708	14.629605
C	4.820180	6.139968	14.699853
C	5.744157	6.807778	13.889179
C	6.545956	6.088731	12.999581
C	8.880443	1.562662	14.141720
C	8.827704	4.032863	14.510817
C	4.582487	4.409986	10.437445
C	6.377870	5.869681	9.412555
H	5.429582	2.935154	13.694127
H	7.274389	6.608154	12.375450
H	3.987821	4.221980	15.261016
H	7.836649	1.473364	14.477915

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H	9.535969	1.461154	15.018801
H	9.098180	0.741778	13.447874
H	5.841619	7.893331	13.947527
H	4.189722	6.705115	15.388774
H	4.332268	3.399977	10.793028
H	3.836994	4.703182	9.684065
H	4.502501	5.106829	11.280145
H	6.379933	6.520754	10.296733
H	5.660767	6.280767	8.686656
H	7.380108	5.884128	8.961784
H	8.935710	5.037851	14.080951
H	9.575386	3.926912	15.309736
H	7.835574	3.949079	14.968787
H	10.873087	2.326379	12.310178
H	11.233095	3.028390	13.903207
H	10.717199	4.086138	12.564117
H	6.911255	3.533793	8.017826
H	5.216750	4.031605	7.798673
H	5.590992	2.554167	8.716828
H	7.260407	1.450395	10.001925
Cl	9.597032	3.346262	9.157777

Int-1

PBE/TZVP Energy : -1411681.79 kcal/mol

Cl	9.233732	0.279024	10.626981
Si	8.308831	2.297104	10.366138
N	7.160807	3.912183	10.370761
N	7.355878	2.414712	11.936119
C	5.385981	3.990120	12.151143
C	4.252952	3.160869	12.117542
H	4.309598	2.192871	11.616898
C	6.632989	3.502426	11.511684
C	5.316586	5.246287	12.768333
H	6.204322	5.878183	12.818839
C	7.532687	1.871871	13.327520
C	6.616376	4.827380	9.331538
C	3.057484	3.593653	12.691937
H	2.174876	2.952297	12.654391
C	6.979120	0.440947	13.380187
H	5.901060	0.437642	13.166636
H	7.134118	0.016023	14.383290
H	7.478805	-0.203136	12.647728
C	4.120405	5.668842	13.352901
H	4.073169	6.643549	13.842142
C	2.989992	4.845481	13.314728
H	2.055880	5.179217	13.770497
C	5.146265	4.523016	8.995906
H	5.013706	3.458488	8.756318
H	4.845596	5.120335	8.122314
H	4.475065	4.778286	9.825608
C	6.776042	6.284996	9.799335
H	6.125157	6.504460	10.654837
H	6.500342	6.965782	8.980618

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H	7.817765	6.487935	10.086429
C	6.824422	2.723930	14.392687
H	7.150936	3.772396	14.359722
H	7.100710	2.316714	15.375495
H	5.732259	2.690406	14.311272
C	9.037019	1.894901	13.661022
H	9.619699	1.272273	12.972878
H	9.187758	1.510088	14.679998
H	9.423557	2.923910	13.619909
C	7.469606	4.624688	8.066547
H	8.534073	4.798192	8.275494
H	7.146613	5.338652	7.296467
H	7.351600	3.611374	7.657729
H	7.693587	1.848961	9.085569
C	3.795671	-0.833669	11.385999
C	4.956273	-0.938375	10.595737
C	5.882756	-1.966860	10.840864
C	5.658581	-2.877504	11.874560
C	4.505690	-2.765349	12.660484
C	3.572458	-1.745687	12.413958
H	3.080019	-0.035933	11.175598
H	6.786611	-2.031672	10.230293
H	6.381490	-3.670706	12.072527
H	4.329465	-3.476456	13.470036
H	2.673838	-1.669569	13.028925
C	5.238003	0.029079	9.521746
H	6.163521	-0.181841	8.934598
O	4.547717	1.012112	9.260576
Cl	10.148926	3.355948	10.246964

TS-1
PBE/TZVP Energy : -1411661.75 kcal/mol

C	7.681667	-3.066554	9.702787
C	7.630406	-1.779453	10.232665
C	6.776871	-0.820864	9.652432
C	5.984660	-1.161198	8.537334
C	6.044302	-2.448431	8.009651
C	6.892886	-3.400052	8.592808
C	6.693682	0.527104	10.200551
O	7.225068	0.831596	11.358761
Si	8.249559	2.266885	10.579298
Cl	9.966702	0.881176	10.618299
N	6.757416	3.452851	10.762236
C	5.807788	4.164119	9.853288
C	5.937960	3.556755	8.445419
N	8.332309	3.177317	12.245320
C	9.109934	2.982593	13.501936
C	10.589674	3.242617	13.162681
C	7.185682	3.824805	11.982775
C	6.470231	4.763811	12.886940
C	5.355162	4.300727	13.600116
C	4.680486	5.157450	14.473062
C	5.108039	6.480460	14.627183
C	6.215155	6.945098	13.908578

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C	6.899377	6.088974	13.043590
C	8.905117	1.534515	13.986630
C	8.716600	3.932557	14.642770
C	4.360358	3.972125	10.339144
C	6.147054	5.662850	9.748387
H	5.027869	3.266276	13.479677
H	7.768627	6.446936	12.488858
H	3.818753	4.789480	15.033076
H	7.846973	1.358059	14.228779
H	9.504861	1.364108	14.892784
H	9.209018	0.808870	13.223210
H	6.550542	7.977337	14.024278
H	4.578304	7.149784	15.307837
H	4.126576	2.903327	10.452989
H	3.665103	4.401710	9.602841
H	4.187831	4.469810	11.301612
H	5.955683	6.191295	10.689472
H	5.521715	6.125343	8.970834
H	7.202667	5.794578	9.473241
H	8.859518	4.986139	14.371886
H	9.375872	3.711310	15.494359
H	7.680421	3.791416	14.974000
H	10.944612	2.573606	12.370157
H	11.205959	3.079549	14.058663
H	10.725047	4.281380	12.828592
H	6.967670	3.628518	8.071944
H	5.281915	4.112927	7.761658
H	5.621706	2.505190	8.414135
H	7.706133	1.500637	9.267027
H	8.239463	-1.491417	11.089726
H	5.324116	-0.411747	8.093745
H	5.431398	-2.716396	7.147492
H	6.938419	-4.409558	8.179240
H	8.337423	-3.815630	10.149843
H	5.858876	1.144575	9.825035
Cl	9.415980	3.765097	9.393201

Int-2

PBE/TZVP Energy : -1411705.73 kcal/mol

C	0.454475	-4.104541	2.398250
C	0.505991	-3.562283	1.112061
C	-0.587585	-3.685724	0.239529
C	-1.732198	-4.364793	0.678844
C	-1.786541	-4.913831	1.965503
C	-0.693514	-4.783161	2.828334
C	-0.532223	-3.075472	-1.139508
O	-0.660113	-1.646093	-1.054199
Si	0.347821	-0.364697	-1.431879
Cl	2.167917	-1.561546	-1.866332
N	-1.003084	0.892559	-0.860644
C	-2.430427	1.193708	-1.152524
C	-2.954563	0.109808	-2.110264
N	1.038728	0.796771	-0.137727
C	2.364604	1.028101	0.520737

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C	3.379396	1.452694	-0.556459
C	-0.131776	1.497438	-0.069052
C	-0.373955	2.753108	0.689547
C	-0.888849	2.725121	1.992400
C	-1.111665	3.921546	2.678088
C	-0.822596	5.146364	2.067075
C	-0.310485	5.174306	0.765132
C	-0.086039	3.981203	0.075122
C	2.791931	-0.280211	1.214016
C	2.336451	2.114296	1.608674
C	-3.266121	1.138958	0.139703
C	-2.572008	2.566789	-1.834676
H	-1.105581	1.768874	2.472069
H	0.317613	3.999396	-0.939038
H	-1.511249	3.895445	3.693391
H	2.052729	-0.560934	1.978685
H	3.762745	-0.130741	1.708701
H	2.895246	-1.106106	0.502835
H	-0.083530	6.127270	0.283858
H	-0.996596	6.079987	2.605305
H	-3.105450	0.182714	0.658143
H	-4.333107	1.222210	-0.113966
H	-3.016253	1.959536	0.822881
H	-2.295624	3.386968	-1.160627
H	-3.618215	2.715836	-2.140067
H	-1.937229	2.614908	-2.730617
H	2.113081	3.111865	1.214005
H	3.340321	2.148080	2.055223
H	1.621641	1.880486	2.407793
H	3.467691	0.696827	-1.345907
H	4.369937	1.594397	-0.099685
H	3.069598	2.404246	-1.013607
H	-2.392012	0.104663	-3.052846
H	-4.008614	0.321708	-2.338472
H	-2.880576	-0.884290	-1.653181
H	0.404645	-3.351530	-1.645661
H	1.402744	-3.038096	0.774448
H	-2.589073	-4.464096	0.007354
H	-2.683637	-5.442705	2.294425
H	-0.733928	-5.209444	3.832871
H	1.312570	-4.004226	3.066365
H	-1.376867	-3.434737	-1.747745
Cl	0.357823	0.470448	-3.420887

TS-2

PBE/TZVP Energy : -1669905.89 kcal/mol

C	-1.964443	1.180150	1.607956
C	-0.991498	1.683044	0.732869
C	-0.759414	3.063168	0.660431
C	-1.495503	3.935293	1.463277
C	-2.467634	3.435122	2.337798
C	-2.700986	2.057957	2.407383
C	-0.242898	0.711119	-0.109249
N	0.858861	0.008993	0.259215

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C	1.882850	0.275648	1.318293
C	3.200408	0.675358	0.626702
Si	0.801422	-1.016568	-1.322966
Cl	2.458281	-2.433524	-1.004311
O	-0.471674	-2.345195	-0.633619
B	-0.529674	-3.147229	-2.298916
O	-1.810409	-3.160479	-2.802834
C	-1.832554	-4.313970	-3.731361
C	-3.235879	-4.898543	-3.722190
C	-0.498260	-3.106475	0.584514
C	-1.728317	-2.775823	1.397126
C	-2.994026	-2.779096	0.789786
C	-4.134770	-2.444793	1.521937
C	-4.027518	-2.111040	2.878348
C	-2.773698	-2.121957	3.496288
C	-1.631262	-2.451110	2.756964
O	0.224958	-4.270317	-2.521971
C	-0.724387	-5.250094	-3.114422
C	-1.240132	-6.113782	-1.964454
C	0.034311	-6.091621	-4.126981
N	-0.616555	0.291935	-1.316020
C	-1.802324	0.642272	-2.144811
C	-1.494369	0.216602	-3.592242
Cl	2.000674	0.205945	-2.718724
C	-3.047851	-0.108500	-1.643911
C	-2.070997	2.158350	-2.154642
C	2.086085	-0.999033	2.155088
C	1.496725	1.402071	2.289689
C	-1.471634	-3.782127	-5.118280
H	-2.135262	0.103737	1.668611
H	-0.004424	3.452549	-0.024930
H	-3.457005	1.661491	3.088245
H	1.163995	-1.245894	2.699903
H	2.882181	-0.827713	2.893773
H	2.376397	-1.851357	1.530133
H	-1.310658	5.009593	1.405616
H	-3.042795	4.119574	2.964425
H	-2.887901	-1.191444	-1.692306
H	-3.910368	0.147937	-2.277566
H	-3.285184	0.168586	-0.607835
H	-2.471348	2.520049	-1.201412
H	-2.815380	2.373890	-2.934562
H	-1.153976	2.717886	-2.389818
H	1.429575	2.377465	1.794130
H	2.290930	1.465746	3.047153
H	0.549910	1.202888	2.807930
H	3.560652	-0.118200	-0.038945
H	3.970241	0.868654	1.388352
H	3.058789	1.588251	0.031089
H	-0.586361	0.711205	-3.961844
H	-2.339404	0.505048	-4.233592
H	-1.371001	-0.869116	-3.677096
H	0.414844	-2.905756	1.160784
H	-0.652777	-2.446519	3.243148
H	-3.075098	-3.022706	-0.271978

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H	-5.111702	-2.440593	1.033559
H	-4.918626	-1.842684	3.449346
H	-2.680259	-1.860618	4.552366
H	-0.484090	-4.176463	0.316687
H	0.195718	-1.843652	-2.534203
H	-0.455462	-3.362795	-5.137920
H	-1.537838	-4.575330	-5.875780
H	-2.179603	-2.986808	-5.388431
H	-0.655514	-6.770426	-4.649585
H	0.543779	-5.467150	-4.870692
H	0.787454	-6.702259	-3.610035
H	-3.939456	-4.174792	-4.156370
H	-3.270289	-5.815695	-4.327457
H	-0.383782	-6.565699	-1.445875
H	-3.567583	-5.136066	-2.704030
H	-1.886099	-6.921490	-2.335648
H	-1.812505	-5.519579	-1.237620

Pdt-1

PBE/TZVP Energy : -1669933.62 kcal/mol

C	-1.217915	3.314643	-0.156591
C	0.010036	3.195638	-0.825829
C	0.496472	4.264658	-1.592600
C	-0.236690	5.449571	-1.680912
C	-1.464497	5.566135	-1.019683
C	-1.954570	4.495961	-0.263247
C	0.783065	1.933668	-0.711915
N	1.376087	1.466335	0.431438
C	1.868798	2.210282	1.638515
C	3.366501	1.894963	1.817067
Si	1.672587	-0.208738	-0.282184
Cl	2.231845	-1.341594	1.565918
O	-1.915508	-1.670395	0.245034
B	-1.335421	-2.903660	0.092219
O	-1.188551	-3.461588	-1.166103
C	-0.335194	-4.648857	-0.984130
C	-0.791854	-5.724195	-1.959949
C	-1.980119	-1.095589	1.557875
C	-2.833652	0.149339	1.555337
C	-3.684340	0.464045	0.488069
C	-4.480970	1.614176	0.532596
C	-4.437892	2.460865	1.644306
C	-3.587551	2.152880	2.713475
C	-2.791364	1.005611	2.667665
O	-0.870055	-3.689415	1.129220
C	-0.560366	-5.003145	0.539230
C	-1.783508	-5.890867	0.775560
C	0.662688	-5.569356	1.246812
N	0.936895	1.007327	-1.646819
C	0.154550	0.771637	-2.892323
C	0.652944	-0.560553	-3.478965
Cl	3.521849	-0.537145	-1.275869
C	-1.347069	0.651411	-2.576207
C	0.406758	1.884641	-3.922905

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C	1.053241	1.753599	2.858972
C	1.743987	3.735869	1.499387
C	1.101438	-4.221903	-1.290620
H	-1.599472	2.482649	0.437796
H	1.458377	4.175258	-2.100276
H	-2.913244	4.576287	0.251145
H	-0.008256	2.004895	2.719969
H	1.414897	2.263771	3.763835
H	1.141172	0.670556	3.011214
H	0.152243	6.283158	-2.268463
H	-2.039033	6.491466	-1.093321
H	-1.522278	-0.123068	-1.815956
H	-1.894925	0.373516	-3.489116
H	-1.758781	1.600614	-2.208139
H	-0.029446	2.839851	-3.606413
H	-0.054912	1.601664	-4.880433
H	1.485178	2.024784	-4.086053
H	2.264519	4.110030	0.607174
H	2.223101	4.185099	2.380690
H	0.703763	4.079426	1.472067
H	3.546267	0.823661	1.960011
H	3.746159	2.426616	2.701638
H	3.935065	2.235529	0.939101
H	1.732011	-0.523793	-3.681020
H	0.126894	-0.758848	-4.423338
H	0.448426	-1.399385	-2.799047
H	-0.960365	-0.850115	1.902534
H	-2.127752	0.772152	3.504392
H	-3.711410	-0.190607	-0.383166
H	-5.133606	1.851610	-0.310259
H	-5.058136	3.358857	1.677315
H	-3.539068	2.811436	3.583065
H	-2.393655	-1.831118	2.269702
H	0.576235	-1.179574	-0.534028
H	1.453713	-3.459263	-0.582284
H	1.786952	-5.079669	-1.249450
H	1.139681	-3.798452	-2.303908
H	0.984069	-6.506328	0.769282
H	1.498207	-4.858857	1.231462
H	0.413558	-5.788677	2.294719
H	-0.598691	-5.392390	-2.989875
H	-0.232951	-6.656344	-1.792452
H	-1.990264	-5.931405	1.853960
H	-1.863915	-5.933442	-1.859045
H	-1.607560	-6.915024	0.418294
H	-2.672846	-5.490117	0.268534

Int-3

PBE/TZVP Energy : -1544056.66 kcal/mol

C	1.284287	-1.288436	3.611502
C	0.161565	-0.569299	3.186582
C	-0.195734	-0.554846	1.836325
C	0.573139	-1.267578	0.910357
C	1.702540	-1.984433	1.326565

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C	2.052342	-1.993094	2.677569
N	0.227488	-1.260872	-0.477078
Si	0.616427	0.372607	-1.802039
Cl	0.905176	1.972862	-3.393408
Cl	2.662565	-0.519128	-2.118010
N	-0.955854	1.248814	-1.124370
C	-0.231583	2.028019	-0.311986
C	-0.748917	3.229158	0.400621
C	-1.303318	3.153680	1.684226
C	-1.774835	4.309574	2.311884
C	-1.696946	5.544811	1.660613
C	-1.145703	5.622173	0.376437
C	-0.673322	4.469322	-0.253065
N	1.043127	1.600354	-0.356311
C	2.278854	2.187163	0.252781
C	2.002012	3.195306	1.382774
C	-2.391596	1.310639	-1.497396
C	-2.747288	2.655888	-2.159635
C	-2.648552	0.189560	-2.518054
C	-3.287577	1.063414	-0.270966
C	3.090253	2.889405	-0.851336
C	3.110794	1.057873	0.886067
C	-0.255015	-2.317910	-1.049138
C	-0.663061	-3.617233	-0.519935
C	-0.935936	-3.914517	0.834171
C	-1.334907	-5.197717	1.200533
C	-1.460452	-6.206990	0.236631
C	-1.207871	-5.923119	-1.109519
C	-0.829298	-4.635728	-1.485474
H	-1.351544	2.195692	2.203597
H	-0.239105	4.523279	-1.253473
H	-2.200329	4.243526	3.314801
H	2.583789	0.632843	1.750067
H	4.066605	1.474615	1.236541
H	3.321638	0.256219	0.172059
H	-1.081313	6.583394	-0.136901
H	-2.064428	6.446932	2.153658
H	-3.053585	0.092646	0.191468
H	-4.342609	1.046427	-0.582217
H	-3.170474	1.851941	0.482914
H	-2.720186	3.483904	-1.440713
H	-3.764342	2.602244	-2.575622
H	-2.042234	2.873671	-2.973890
H	1.542139	4.125352	1.032053
H	2.972182	3.450132	1.833396
H	1.370573	2.760565	2.169637
H	3.367131	2.184426	-1.644678
H	4.007952	3.314146	-0.417315
H	2.505231	3.701834	-1.304617
H	-2.050519	0.332620	-3.428040
H	-3.711570	0.196940	-2.796581
H	-2.416000	-0.797799	-2.095476
H	0.010024	-0.530703	-2.825728
H	-0.849224	-3.144641	1.597794
H	-0.645707	-4.407954	-2.538217

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H	-1.315660	-6.701834	-1.866381
H	-1.763954	-7.211917	0.536415
H	-1.549702	-5.414141	2.248581
H	-0.368952	-2.214313	-2.136417
H	-1.080647	-0.018831	1.494460
H	2.300413	-2.519048	0.587104
H	-0.444446	-0.020270	3.910148
H	2.933884	-2.550193	3.000126
H	1.561291	-1.297573	4.667088

TS-3

PBE/TZVP Energy : -1544024.87 kcal/mol

C	7.496506	-3.209226	9.584067
C	7.531709	-1.904399	10.065689
C	6.587501	-0.958644	9.610648
C	5.635776	-1.340303	8.641218
C	5.599955	-2.650200	8.167688
C	6.528671	-3.586222	8.640800
C	6.621468	0.427431	10.057985
Si	8.206504	2.296145	10.555340
Cl	9.994854	0.978468	10.465715
N	6.768771	3.575149	10.868134
C	5.456972	3.939531	10.271776
C	5.548116	3.654696	8.761263
N	8.511178	3.288498	12.154551
C	9.703848	3.618275	13.007254
C	10.782500	4.257877	12.114027
C	7.354502	3.977267	11.994825
C	6.767648	4.958995	12.946618
C	5.929241	4.489073	13.966482
C	5.338584	5.392070	14.855068
C	5.586134	6.762713	14.729202
C	6.427221	7.230905	13.712480
C	7.015686	6.333048	12.821532
C	10.254890	2.332428	13.643343
C	9.399369	4.578444	14.169565
C	4.328931	3.110924	10.915153
C	5.120539	5.436698	10.417165
H	5.747411	3.416908	14.066756
H	7.666620	6.695934	12.023959
H	4.685895	5.022319	15.648140
H	9.521725	1.904398	14.340417
H	11.164889	2.578028	14.209510
H	10.516471	1.584861	12.886810
H	6.624241	8.299867	13.612327
H	5.124534	7.467346	15.423679
H	4.498973	2.032547	10.799907
H	3.366582	3.356885	10.442509
H	4.252278	3.330821	11.989075
H	4.851397	5.711428	11.442417
H	4.257749	5.660016	9.772883
H	5.963378	6.061716	10.090669
H	9.158231	5.592766	13.835193
H	10.307305	4.638648	14.786662

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H	8.581744	4.213452	14.805387
H	11.089149	3.575147	11.311336
H	11.665002	4.503256	12.723971
H	10.406264	5.181027	11.651034
H	6.329807	4.273684	8.301410
H	4.583133	3.885779	8.289441
H	5.786675	2.606741	8.538442
H	7.647737	1.503281	9.250784
H	8.290765	-1.596214	10.785152
H	4.921287	-0.600785	8.270697
H	4.854935	-2.943787	7.426221
H	6.505476	-4.611561	8.266398
H	8.227347	-3.939458	9.935886
H	5.877868	1.067059	9.568117
Cl	9.153598	3.775524	9.106204
N	7.196409	0.820926	11.243175
C	6.933718	0.134504	12.439723
C	5.618891	-0.273070	12.747567
C	7.965203	-0.163234	13.347651
C	5.349424	-0.964336	13.929390
H	4.808038	-0.030122	12.057821
C	7.686843	-0.838168	14.535157
H	8.985541	0.105542	13.086643
C	6.379488	-1.243916	14.834603
H	4.325414	-1.272317	14.151690
H	8.501583	-1.067369	15.225771
H	6.166933	-1.775514	15.763976

Int-4

PBE/TZVP Energy : -1544077.59 kcal/mol

C	1.574105	-5.248630	0.349526
C	1.069393	-4.022160	-0.091094
C	-0.114570	-3.967248	-0.839192
C	-0.786096	-5.161882	-1.134772
C	-0.281357	-6.391470	-0.699143
C	0.901430	-6.438318	0.046501
C	-0.654324	-2.648770	-1.361446
Si	0.249410	-0.014082	-1.214157
Cl	2.054677	-1.021854	-2.048667
N	-1.062904	1.235945	-0.462635
C	-2.533291	1.479475	-0.526165
C	-3.193004	0.235360	-1.146191
N	1.095112	1.361539	-0.277376
C	2.509844	1.737206	0.058786
C	3.227315	2.159461	-1.235499
C	-0.084634	2.010101	-0.028092
C	-0.236337	3.355769	0.581195
C	-0.511601	3.490964	1.948475
C	-0.647565	4.763402	2.507089
C	-0.517989	5.901241	1.703325
C	-0.250076	5.765373	0.336795
C	-0.106040	4.495536	-0.225982
C	3.195260	0.522231	0.715516
C	2.614914	2.889802	1.071739
C	-3.116181	1.672144	0.886312

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C	-2.845696	2.700933	-1.409518
H	-0.609138	2.602188	2.574182
H	0.110149	4.385926	-1.290394
H	-0.856050	4.865250	3.573615
H	2.727081	0.294999	1.685028
H	4.251892	0.763331	0.900902
H	3.153599	-0.371539	0.085388
H	-0.149434	6.650147	-0.294153
H	-0.625687	6.894880	2.142349
H	-2.816784	0.843980	1.543852
H	-4.213733	1.687904	0.821418
H	-2.792108	2.617833	1.336725
H	-2.470642	3.630183	-0.962638
H	-3.935392	2.796485	-1.525418
H	-2.398160	2.579526	-2.405712
H	2.260906	3.847357	0.675083
H	3.679718	3.002656	1.319881
H	2.076236	2.670504	2.003199
H	3.222142	1.352256	-1.977606
H	4.272267	2.422862	-1.014301
H	2.733501	3.041198	-1.669887
H	-2.818545	0.037877	-2.158011
H	-4.276053	0.409510	-1.210330
H	-3.028278	-0.650908	-0.521547
H	-0.177972	-2.433870	-2.329572
H	1.590403	-3.092823	0.145635
H	-1.718458	-5.128548	-1.705995
H	-0.817691	-7.313332	-0.934843
H	1.294265	-7.396157	0.394049
H	2.497100	-5.276438	0.933201
H	-1.733007	-2.749908	-1.578115
Cl	-0.398512	0.492286	-3.207464
N	-0.406983	-1.499747	-0.480434
C	-0.948899	-1.544326	0.818681
C	-2.032098	-2.386451	1.150955
C	-0.393037	-0.756723	1.848219
C	-2.558936	-2.394638	2.444933
H	-2.473483	-3.039249	0.398804
C	-0.932837	-0.758726	3.133333
H	0.486826	-0.148876	1.635294
C	-2.027331	-1.574173	3.444698
H	-3.401608	-3.052860	2.668278
H	-0.480061	-0.130500	3.904100
H	-2.445063	-1.583740	4.452862

TS-4

PBE/TZVP Energy : -1802264.03 kcal/mol

C	-1.548922	-1.100109	1.257421
C	-1.562816	-1.653915	-0.033502
C	-2.786218	-1.749714	-0.709406
C	-3.964356	-1.285021	-0.117556
C	-3.939210	-0.713847	1.157911
C	-2.722830	-0.624280	1.844107
N	-0.357739	-2.228710	-0.607290

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C	0.149008	-3.352772	0.252865
C	-0.916044	-4.197319	0.921391
C	-0.724234	-4.585809	2.255814
C	-1.635692	-5.427829	2.901735
C	-2.766573	-5.888567	2.220905
C	-2.974941	-5.498870	0.892885
C	-2.057246	-4.664470	0.251439
Si	0.878298	-0.977848	-1.275573
Cl	2.031001	0.006501	-2.961890
N	1.139766	0.292487	0.073400
C	2.107158	0.515198	1.193775
C	3.443361	0.978908	0.585619
C	0.208512	1.121150	-0.454385
N	-0.378592	0.505520	-1.483581
C	-1.271604	1.122201	-2.525146
C	-1.559788	0.058315	-3.591789
C	-0.069319	2.506837	0.007088
C	-1.154372	2.771087	0.853373
C	-1.382688	4.072771	1.305224
C	-0.536512	5.113590	0.907822
C	0.542778	4.850901	0.056469
C	0.779909	3.550018	-0.391400
C	2.313969	-0.806248	1.956876
C	1.616172	1.541372	2.231232
C	-2.604901	1.581099	-1.906452
C	-0.598042	2.320753	-3.222863
Cl	2.617339	-2.314914	-1.084011
B	-0.207106	-2.969165	-2.828242
O	0.656285	-4.041028	-2.964471
C	-0.103097	-5.159055	-3.551027
C	0.768143	-5.778386	-4.640182
O	-1.505774	-3.244087	-3.244901
C	-1.406046	-4.442508	-4.093875
C	-1.256630	-3.931576	-5.530570
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Pdt-2

PBE/TZVP Energy : -1802309.46 kcal/mol

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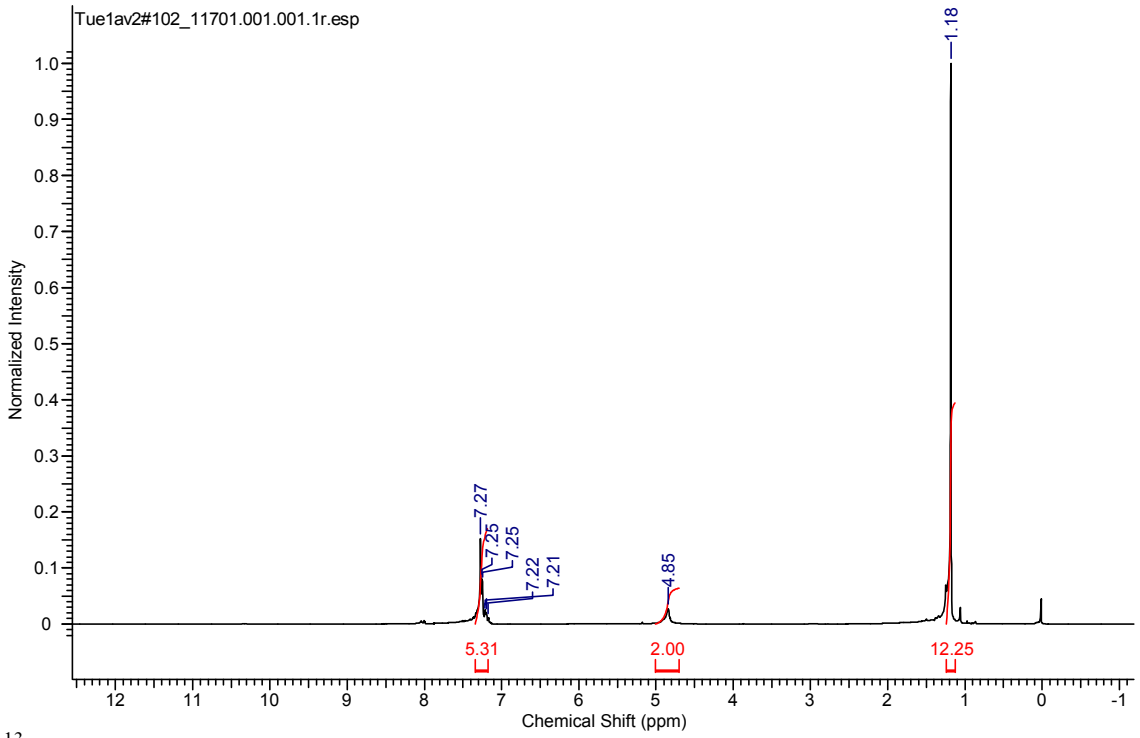
^{1}H NMR Spectrum of **2** ($CDCl_3$, 200 MHz, 298 K)



^{13}C NMR spectrum of **2** ($CDCl_3$, 50.28 MHz, 298 K)

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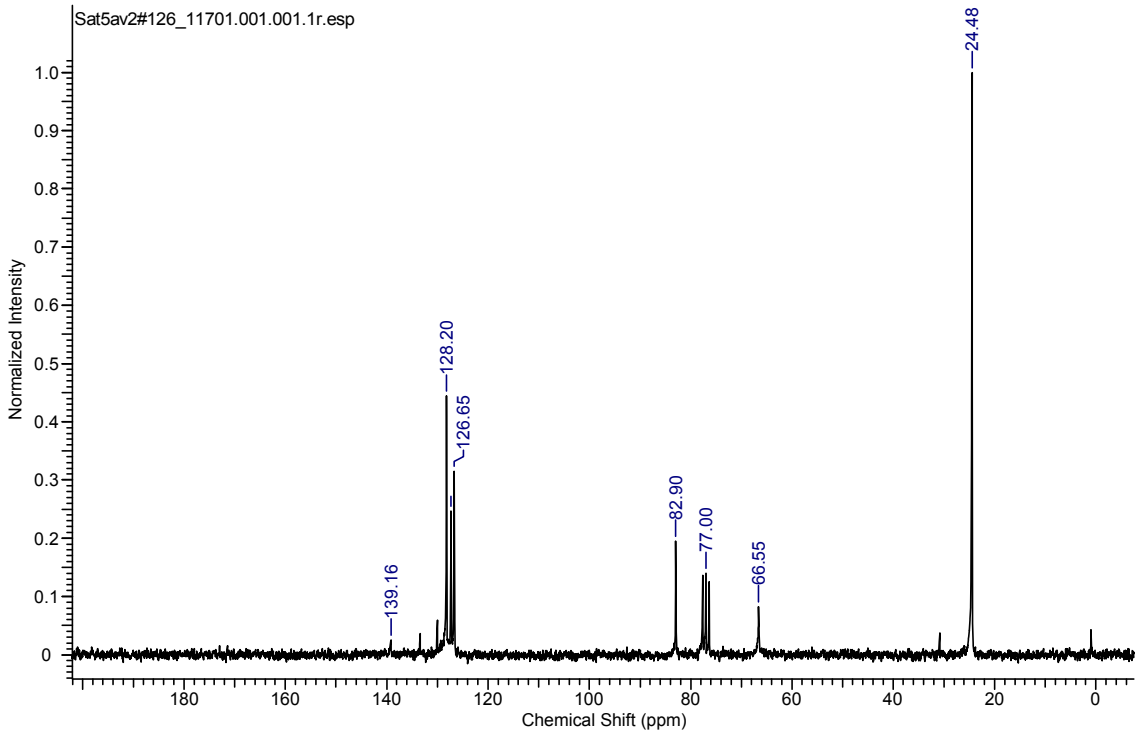
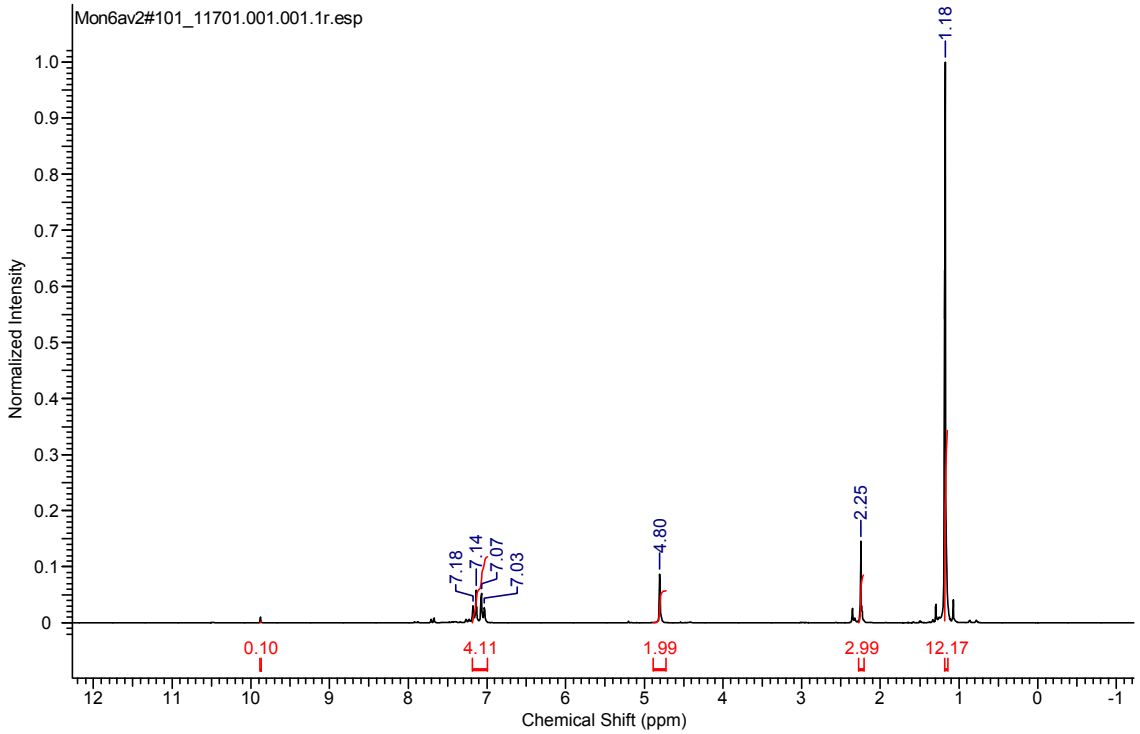


^{1}H NMR Spectrum of **3** ($CDCl_3$, 200 MHz, 298 K)



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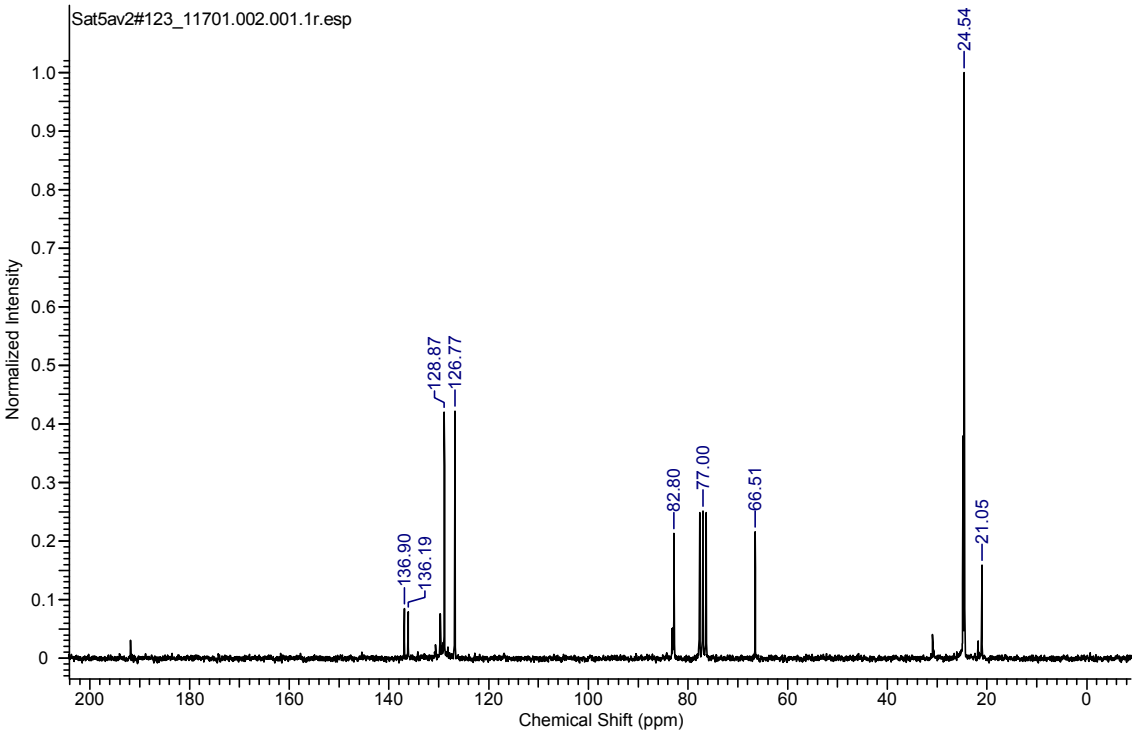
^{13}C NMR spectrum of **3** ($CDCl_3$, 50.28 MHz, 298 K)



^{1}H NMR Spectrum of **4** ($CDCl_3$, 200 MHz, 298 K)

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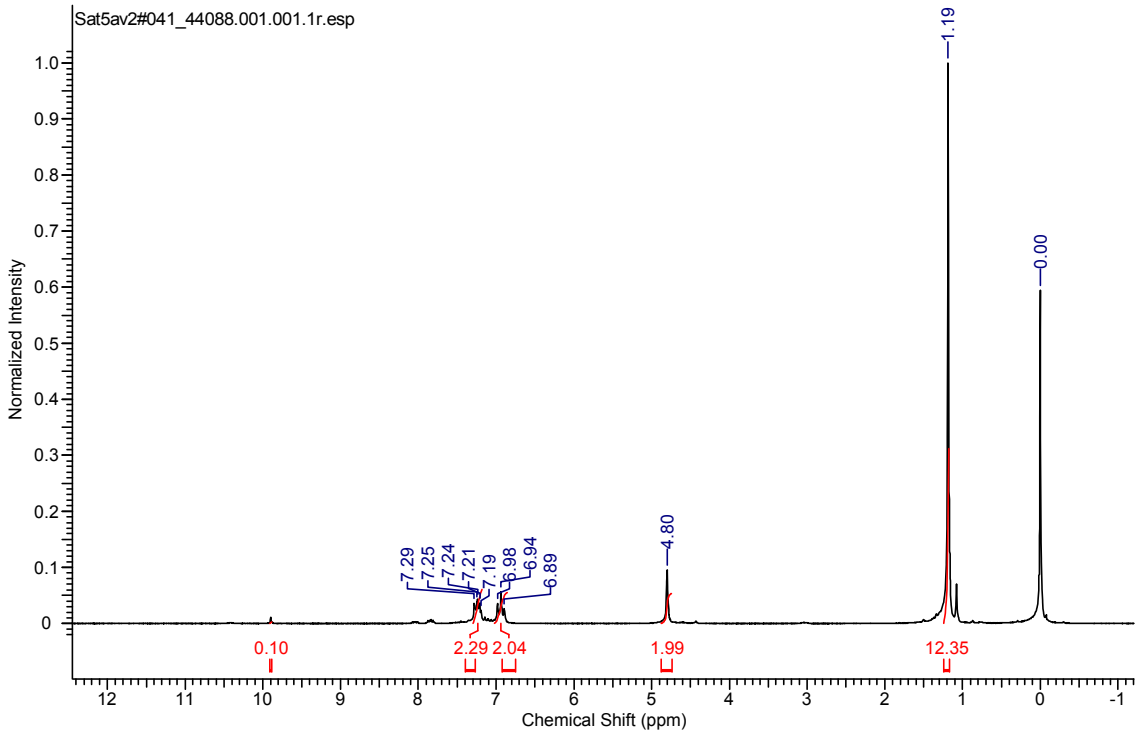
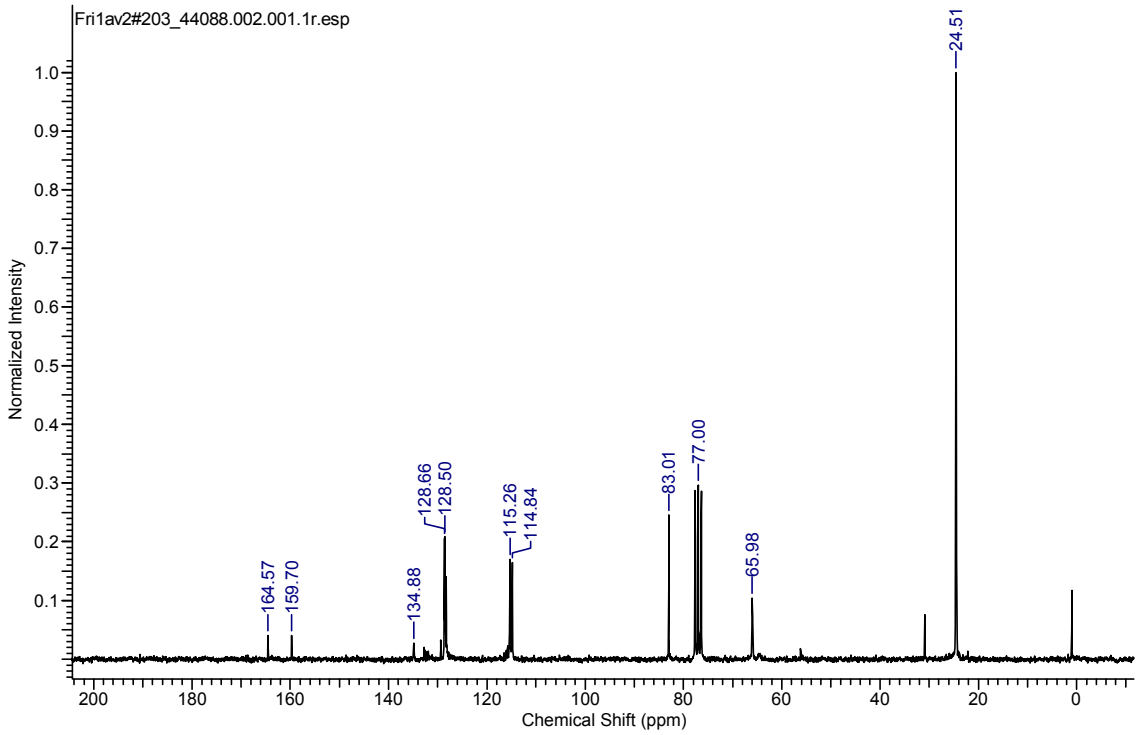


^{13}C NMR spectrum of **4** ($CDCl_3$, 50.28 MHz, 298 K)



^{1}H NMR Spectrum of **5** ($CDCl_3$, 200 MHz, 298 K)

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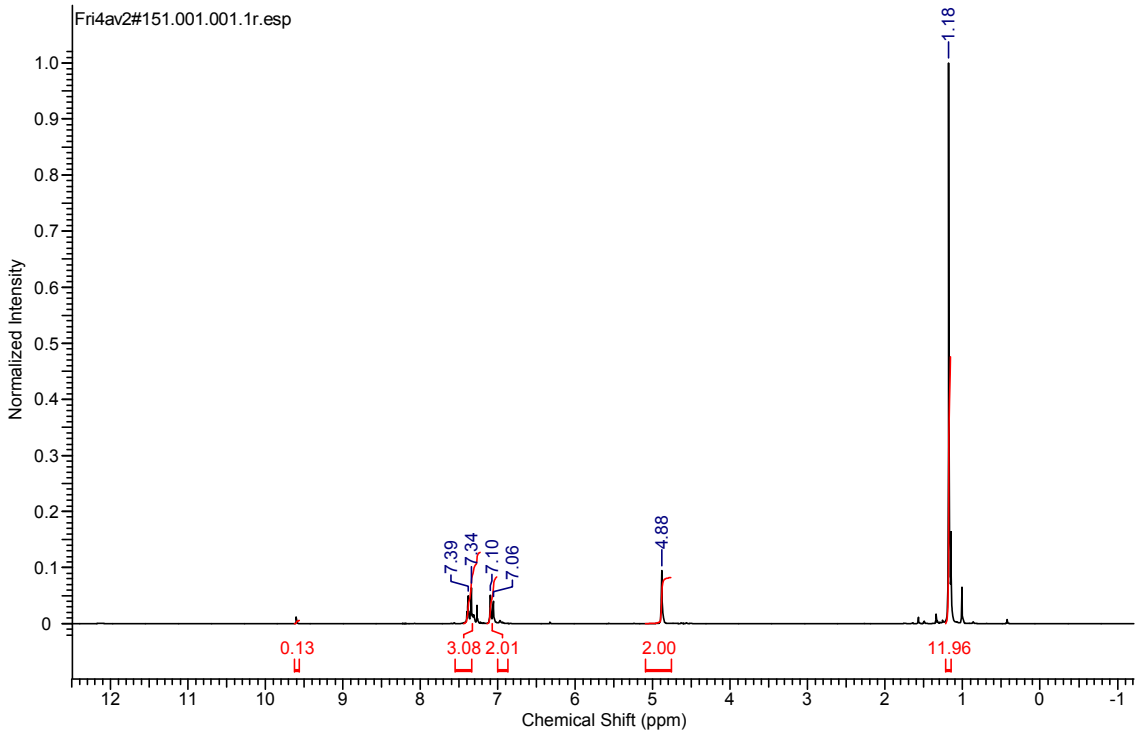
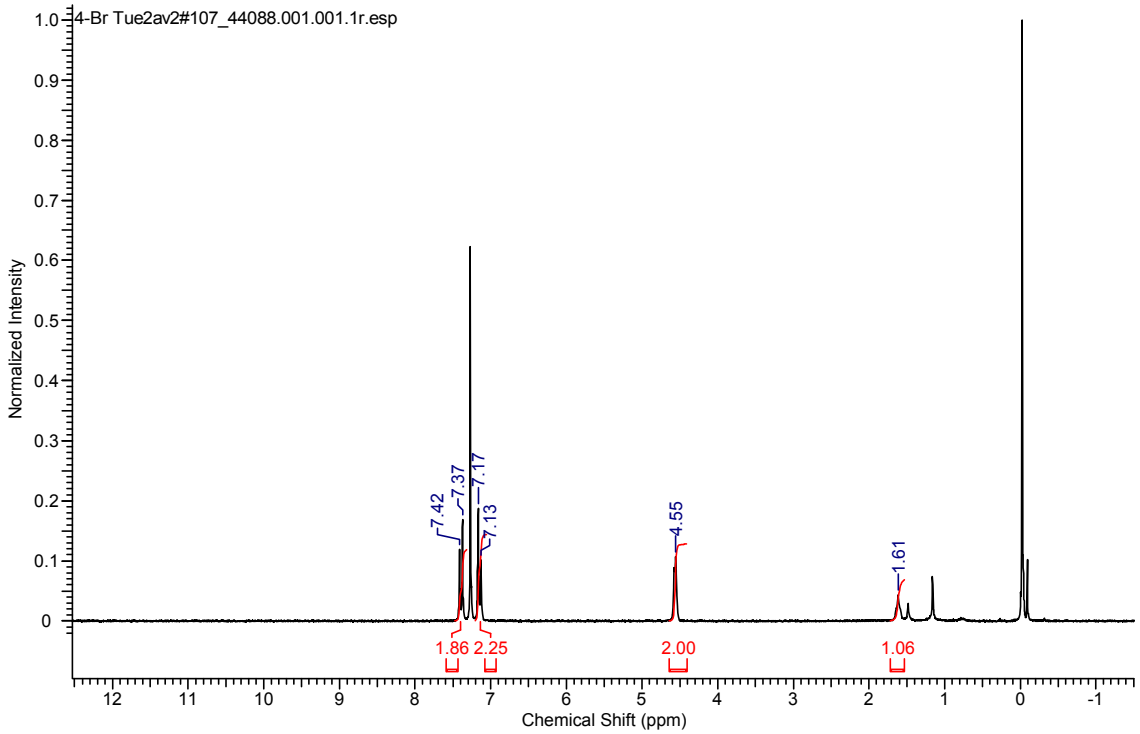


^{1}H NMR Spectrum of **5' (Isolated)** ($CDCl_3$, 200 MHz, 298 K)



^{13}C NMR spectrum of **5' (Isolated)** ($CDCl_3$, 50.28 MHz, 298 K)

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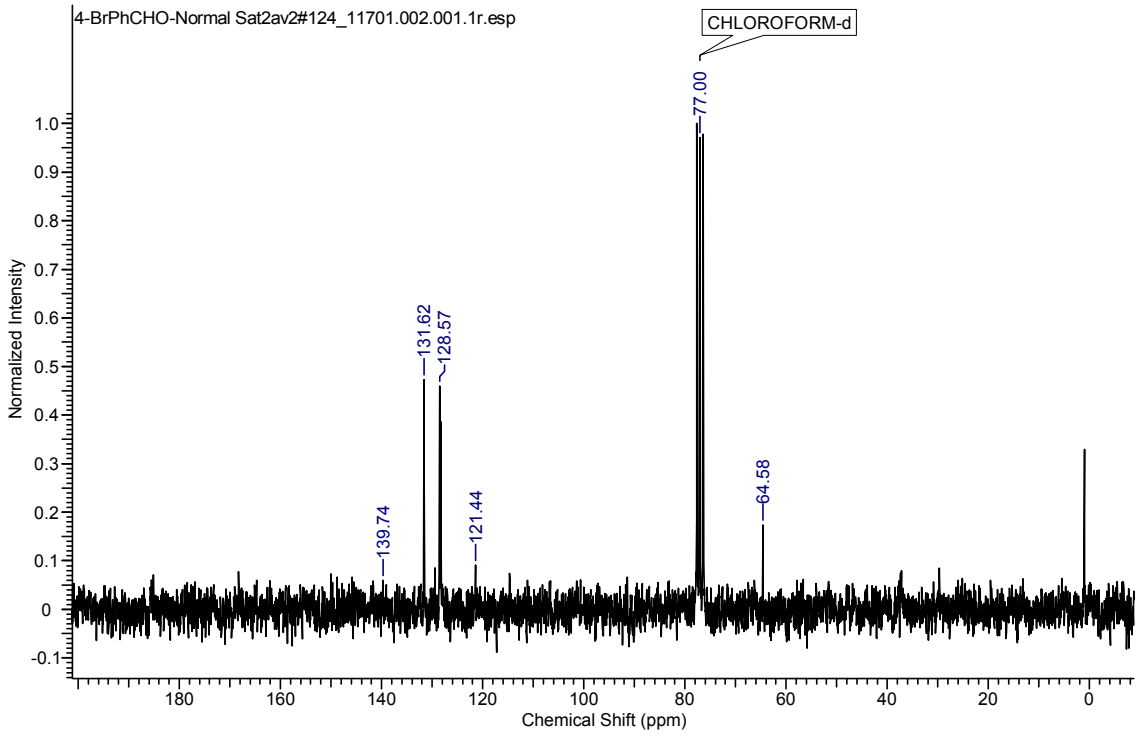
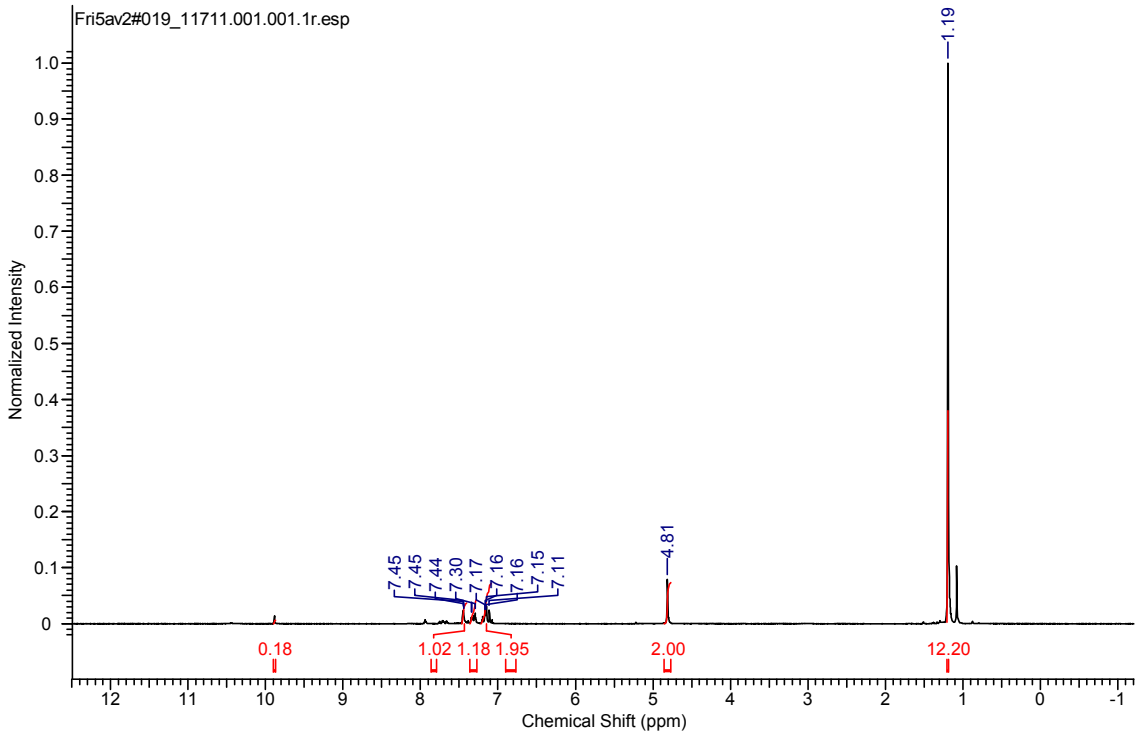


^{1}H NMR Spectrum of **6** ($CDCl_3$, 200 MHz, 298 K)



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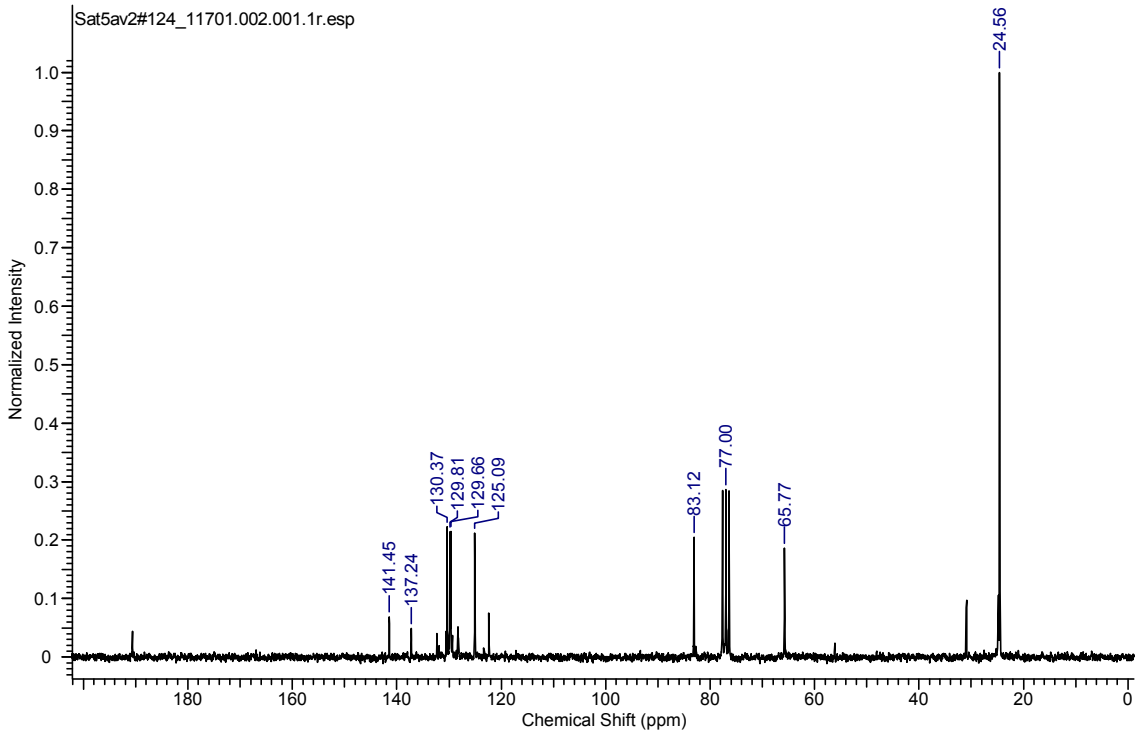
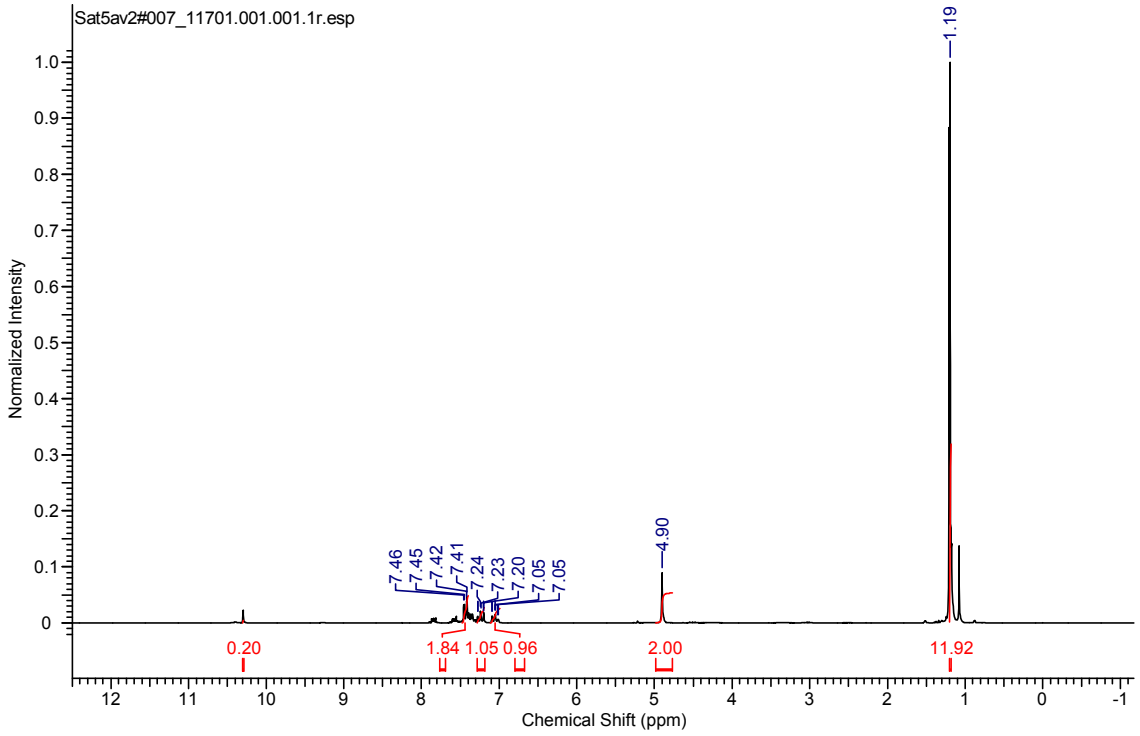
^{13}C NMR spectrum of **6** ($CDCl_3$, 50.28 MHz, 298 K)



^{1}H NMR Spectrum of **7** ($CDCl_3$, 200 MHz, 298 K)



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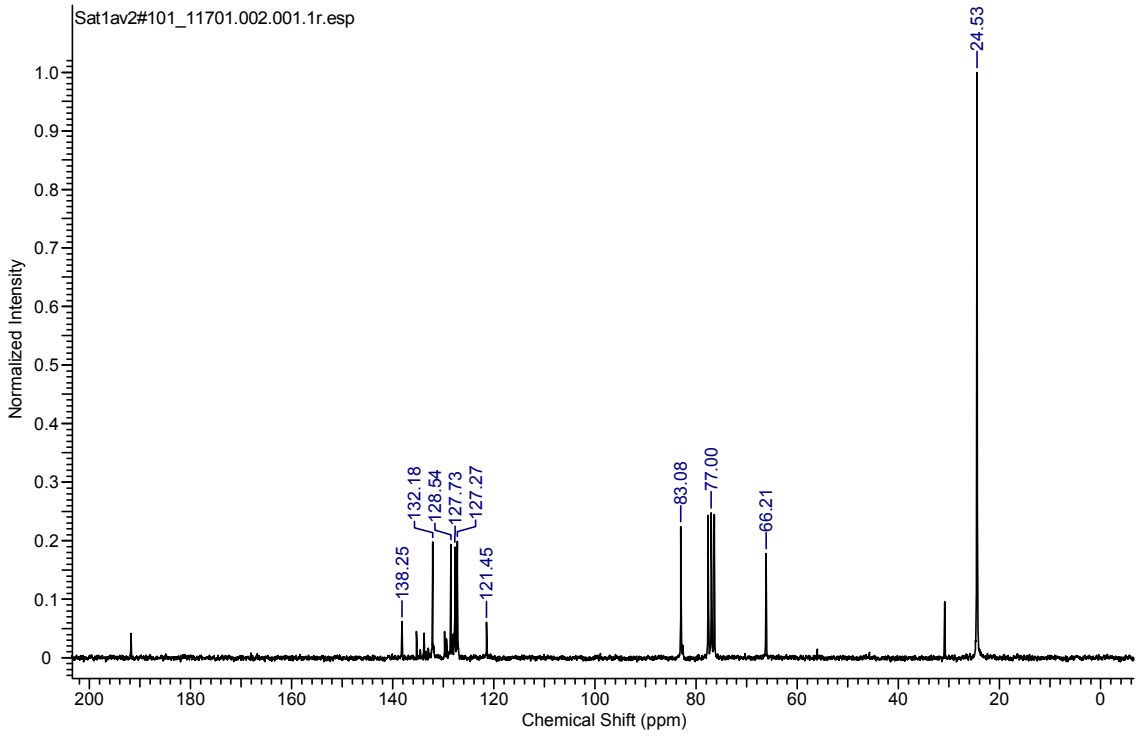
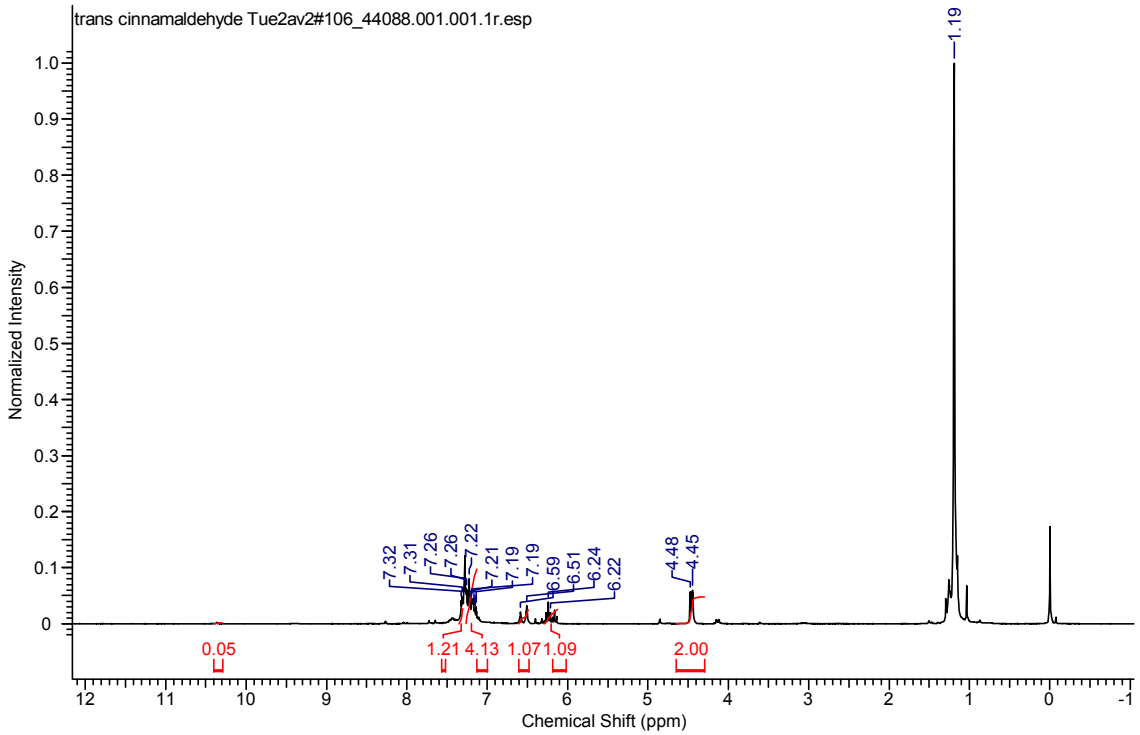
^{13}C NMR spectrum of **7** ($CDCl_3$, 50.28 MHz, 298 K)



^{1}H NMR Spectrum of **8** ($CDCl_3$, 200 MHz, 298 K)



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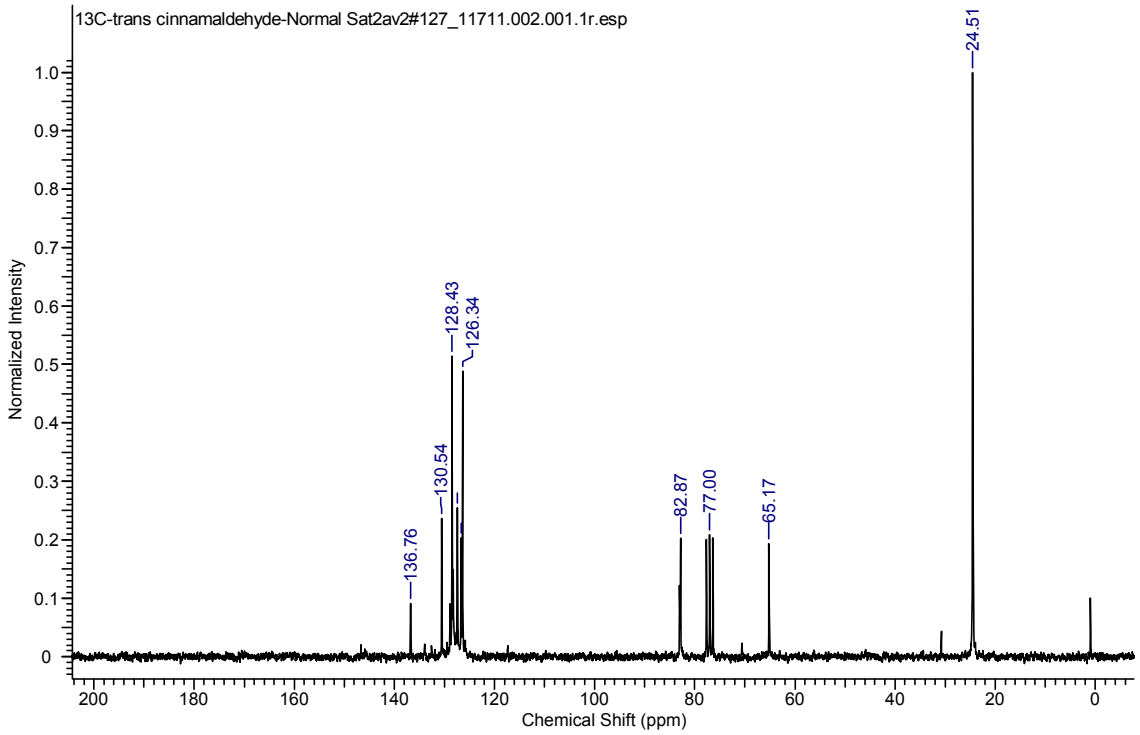
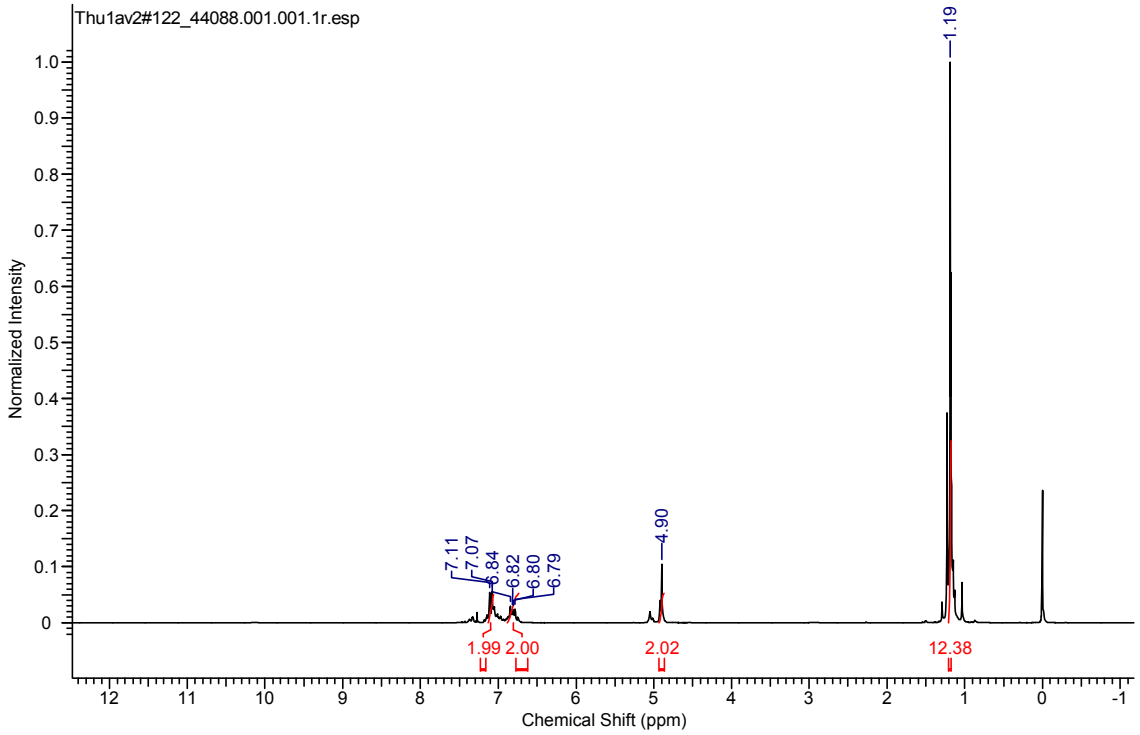
^{13}C NMR spectrum of **8** ($CDCl_3$, 50.28 MHz, 298 K)



^{1}H NMR Spectrum of **9** ($CDCl_3$, 200 MHz, 298 K)



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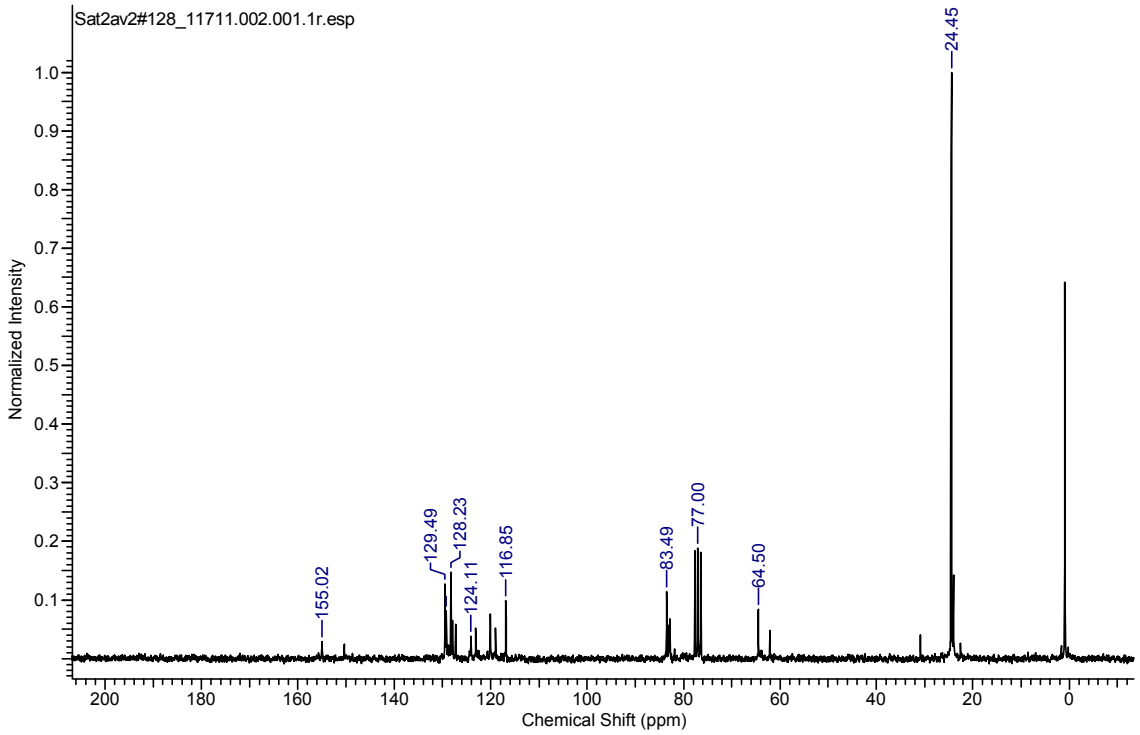
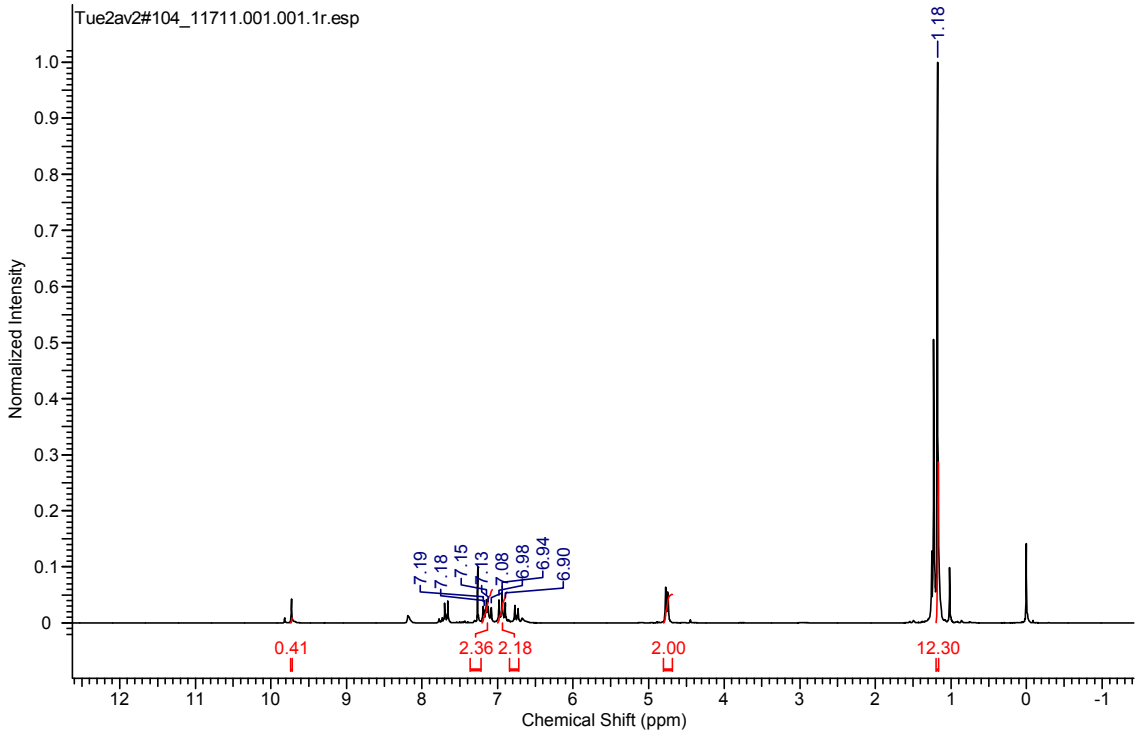
^{13}C NMR spectrum of **9** ($CDCl_3$, 50.28 MHz, 298 K)



^{1}H NMR Spectrum of **10** ($CDCl_3$, 200 MHz, 298 K)



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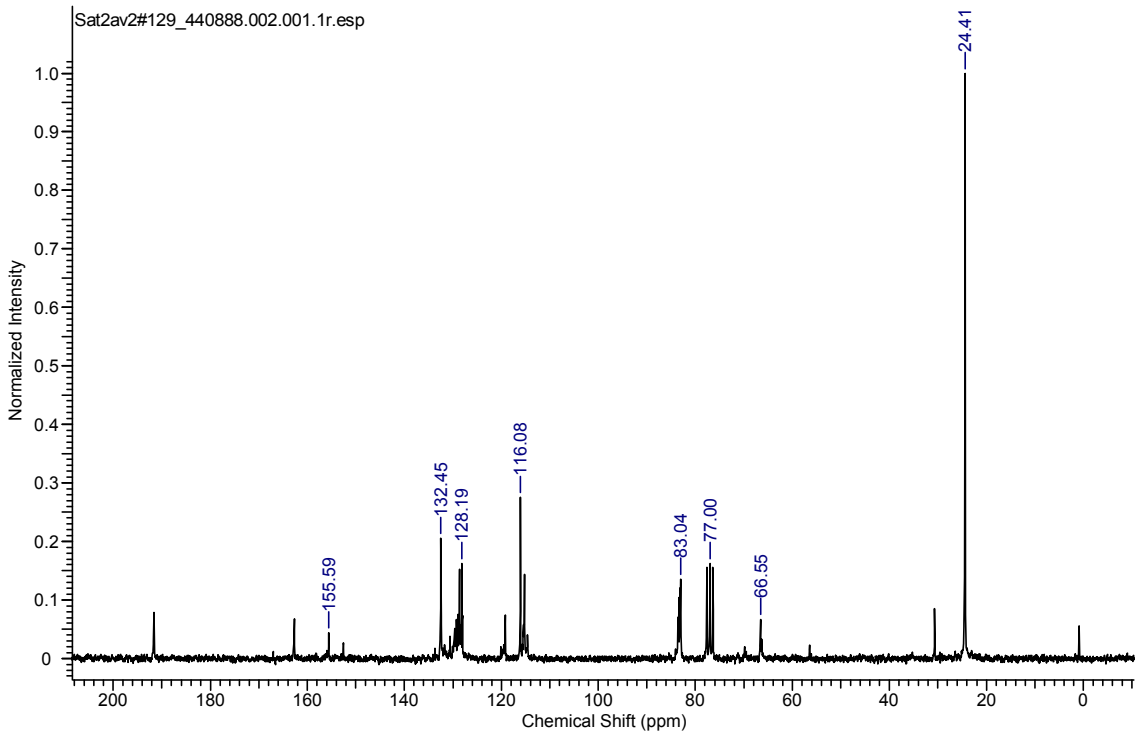
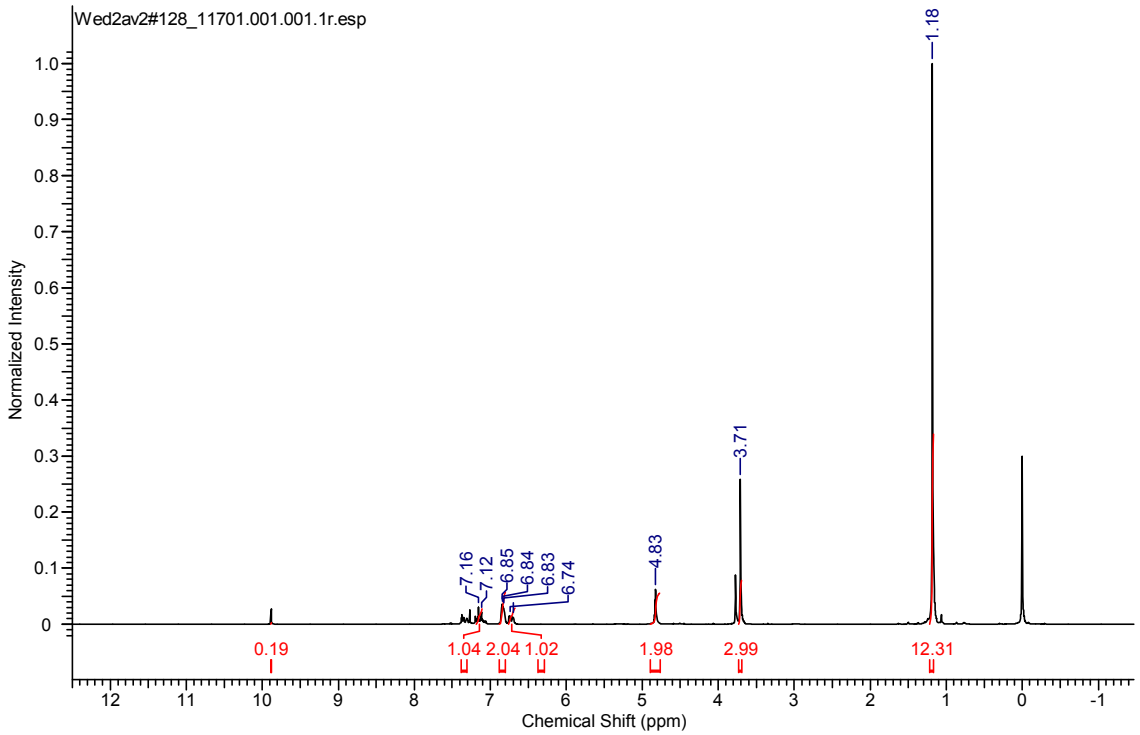
DOI: 10.1039/C6DT04893E

^{13}C NMR spectrum of **10** ($CDCl_3$, 50.28 MHz, 298 K)



^{1}H NMR Spectrum of **11** ($CDCl_3$, 200 MHz, 298 K)



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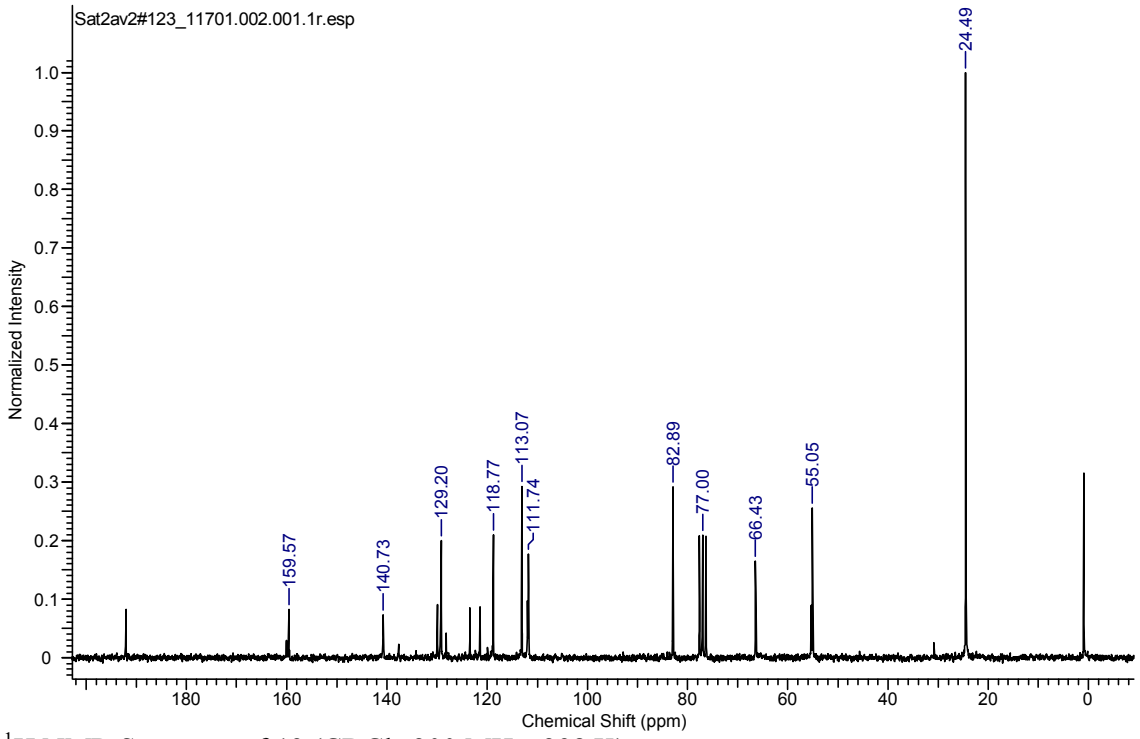
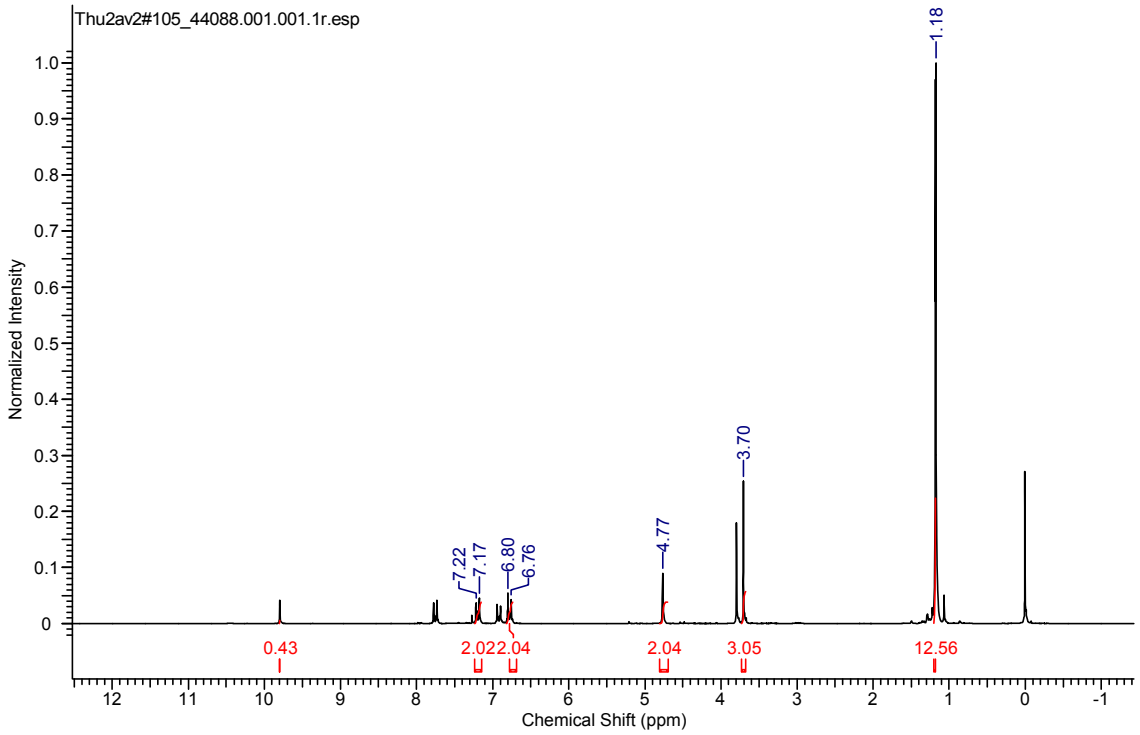
^{13}C NMR spectrum of **11** ($CDCl_3$, 50.28 MHz, 298 K)



^{1}H NMR Spectrum of **12** ($CDCl_3$, 200 MHz, 298 K)



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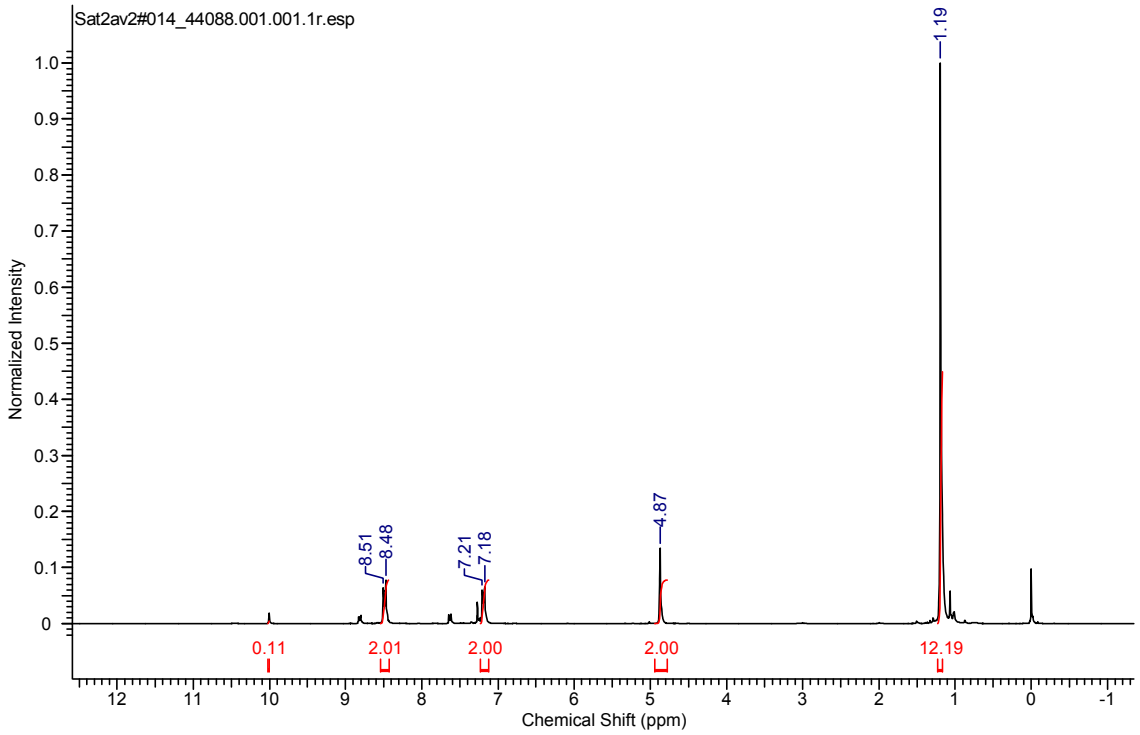
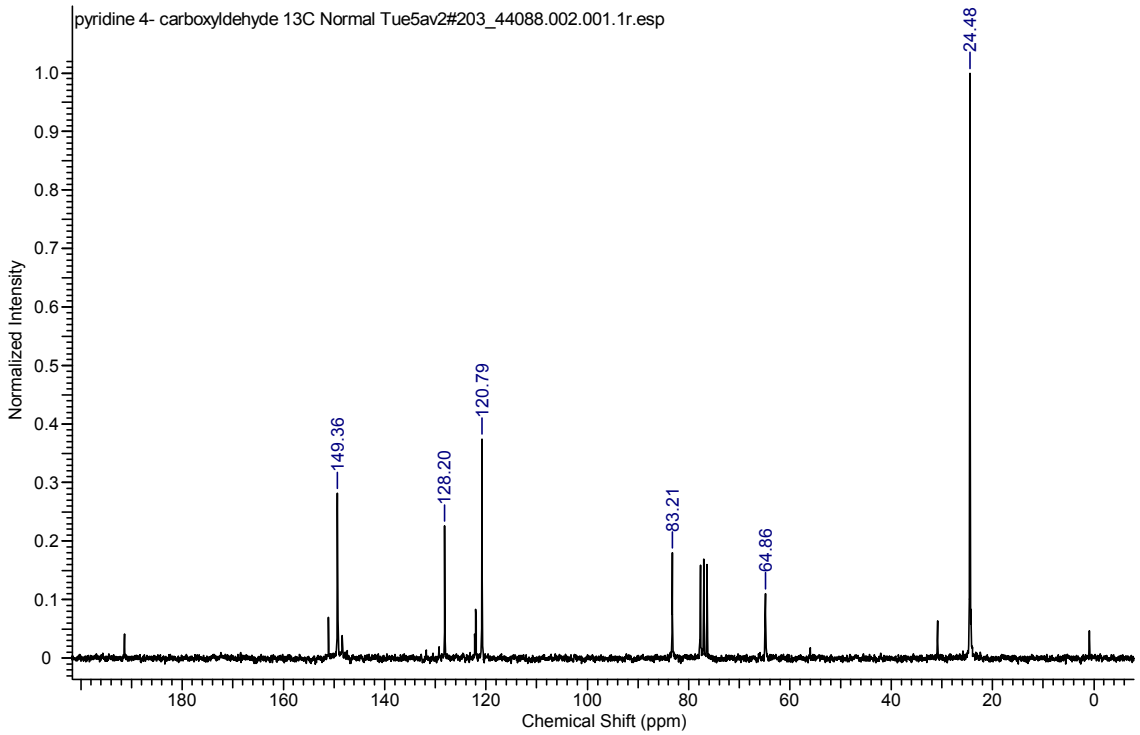
^{1}H NMR Spectrum of **13** ($CDCl_3$, 200 MHz, 298 K)



^{13}C NMR spectrum of **13** ($CDCl_3$, 50.28 MHz, 298 K)



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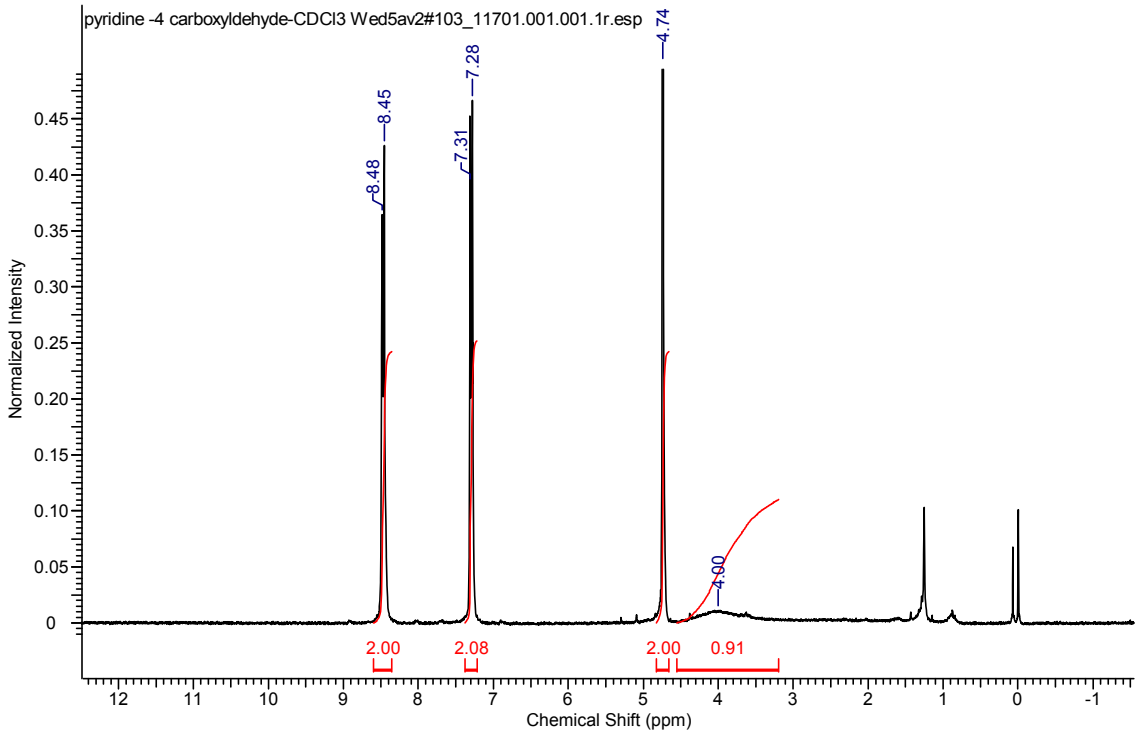
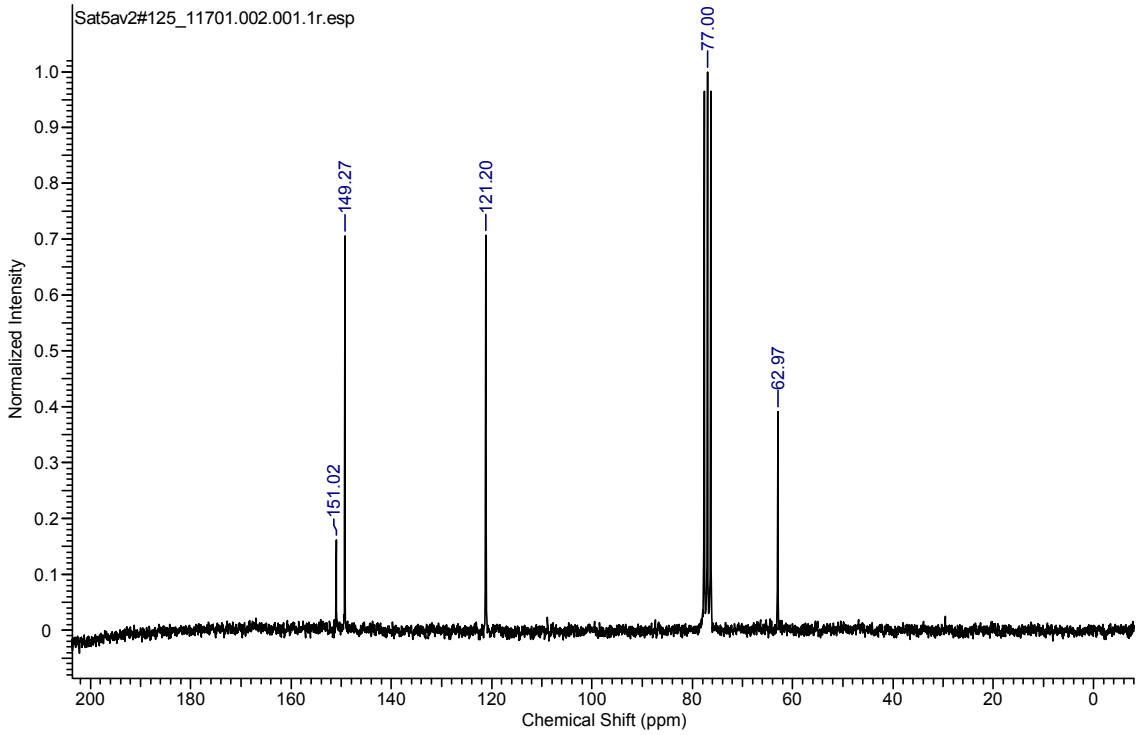
^{1}H NMR Spectrum of **13' (Isolated)** ($CDCl_3$, 200 MHz, 298 K)



^{13}C NMR spectrum of **13' (Isolated)** ($CDCl_3$, 50.28 MHz, 298 K)



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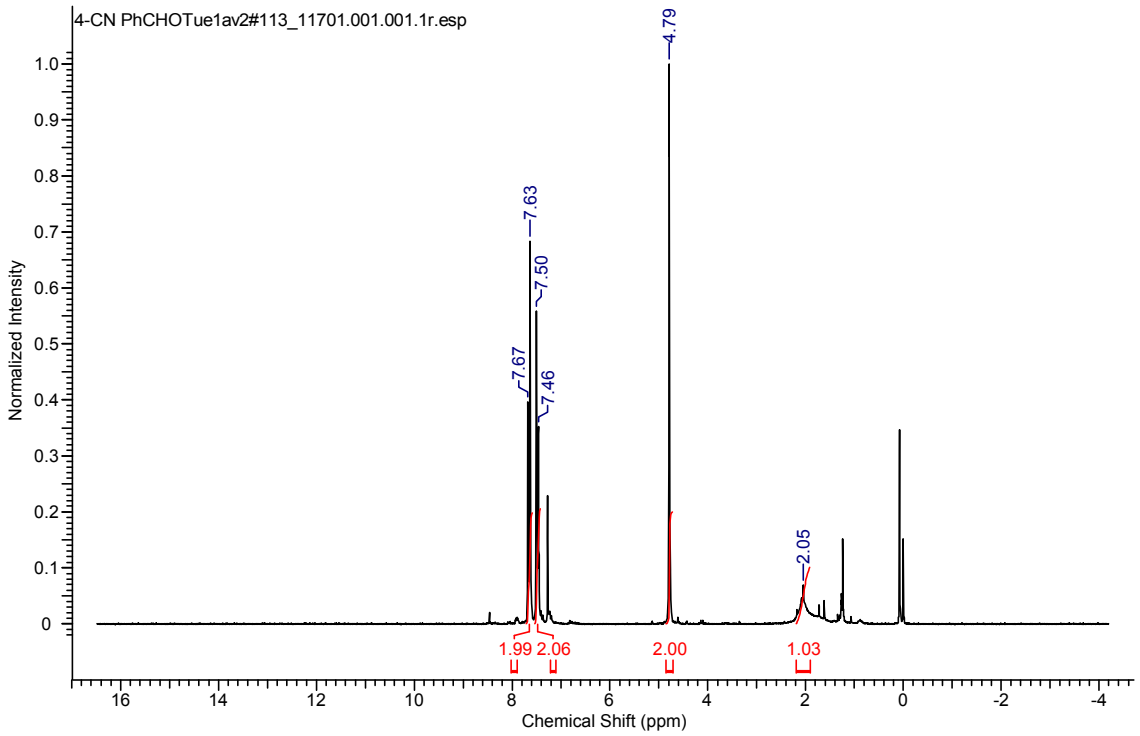
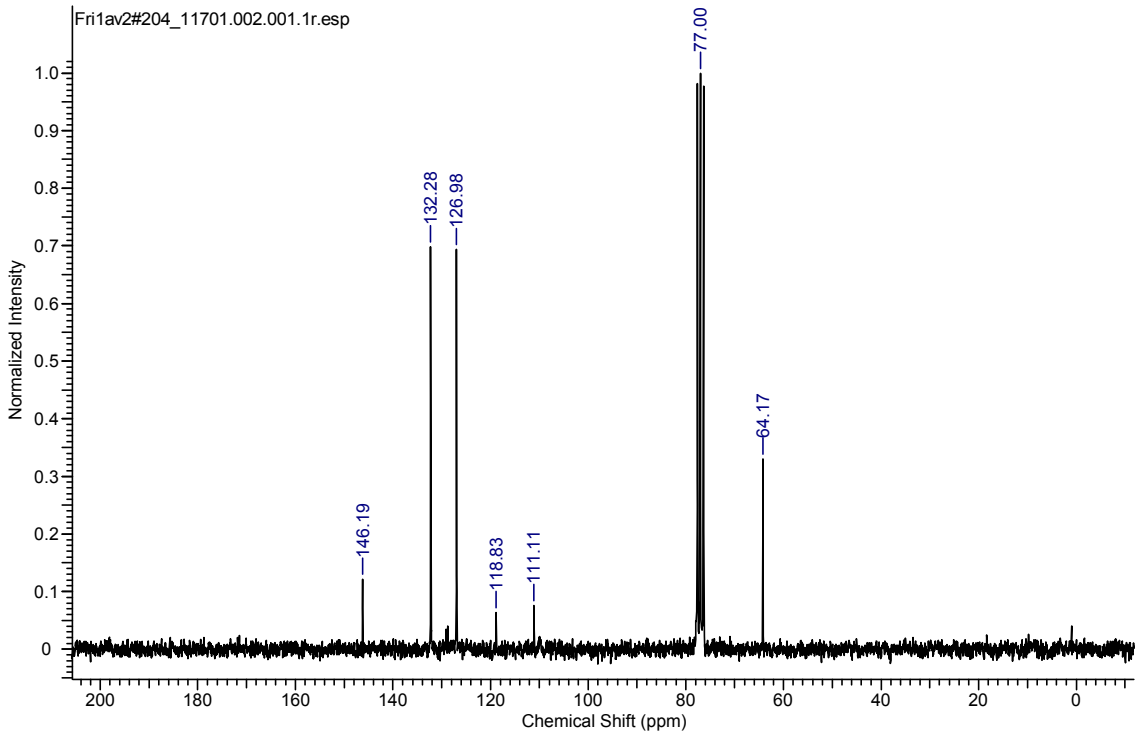
^{1}H NMR Spectrum of **14' (Isolated)** ($CDCl_3$, 200 MHz, 298 K)



^{13}C NMR spectrum of **14' (Isolated)** ($CDCl_3$, 50.28 MHz, 298 K)



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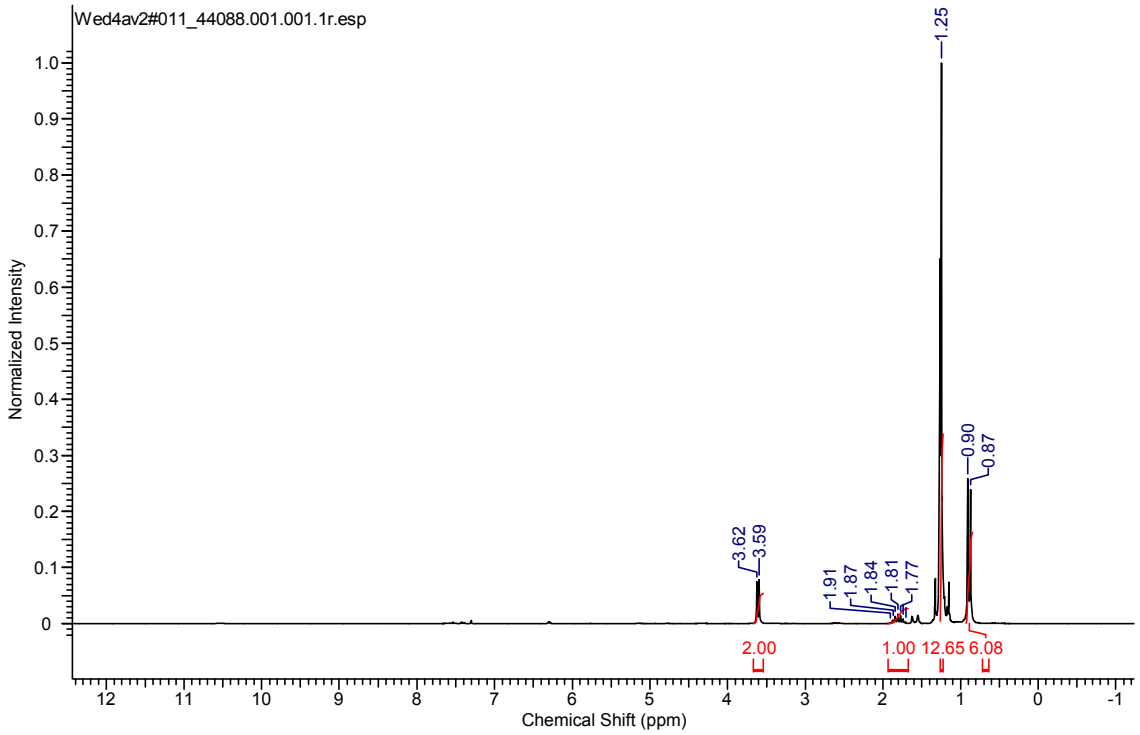
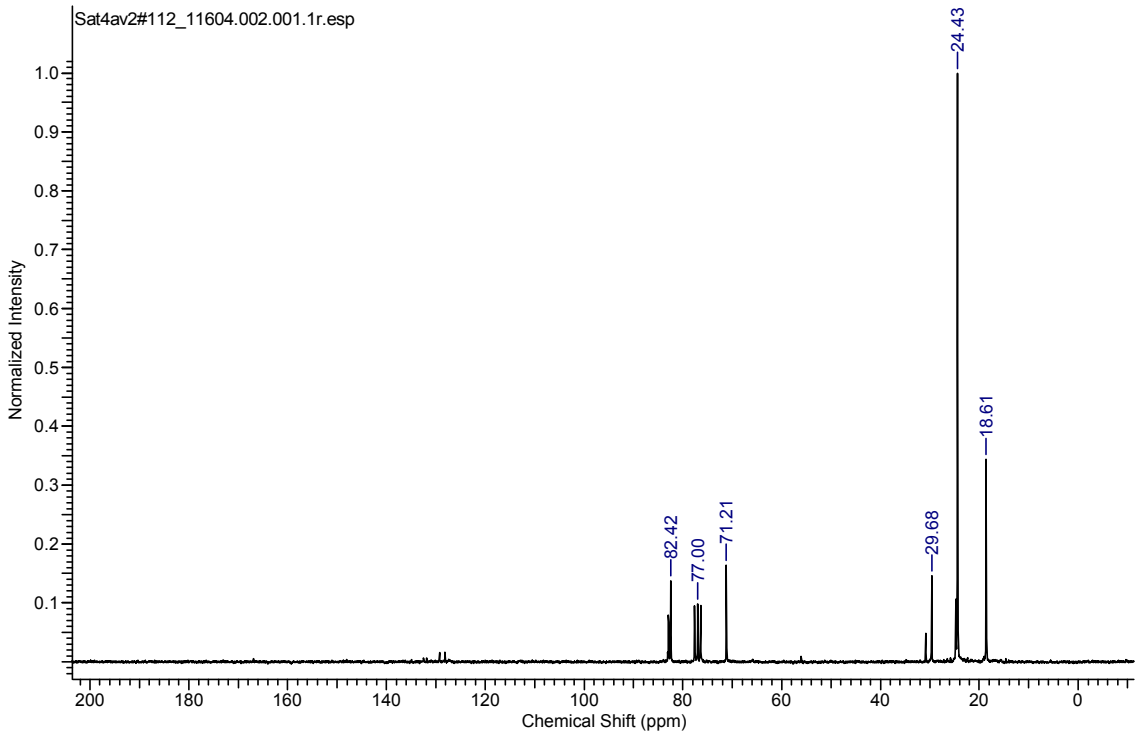
^{1}H NMR Spectrum of **15** ($CDCl_3$, 200 MHz, 298 K)



^{13}C NMR spectrum of **15** ($CDCl_3$, 50.28 MHz, 298 K)



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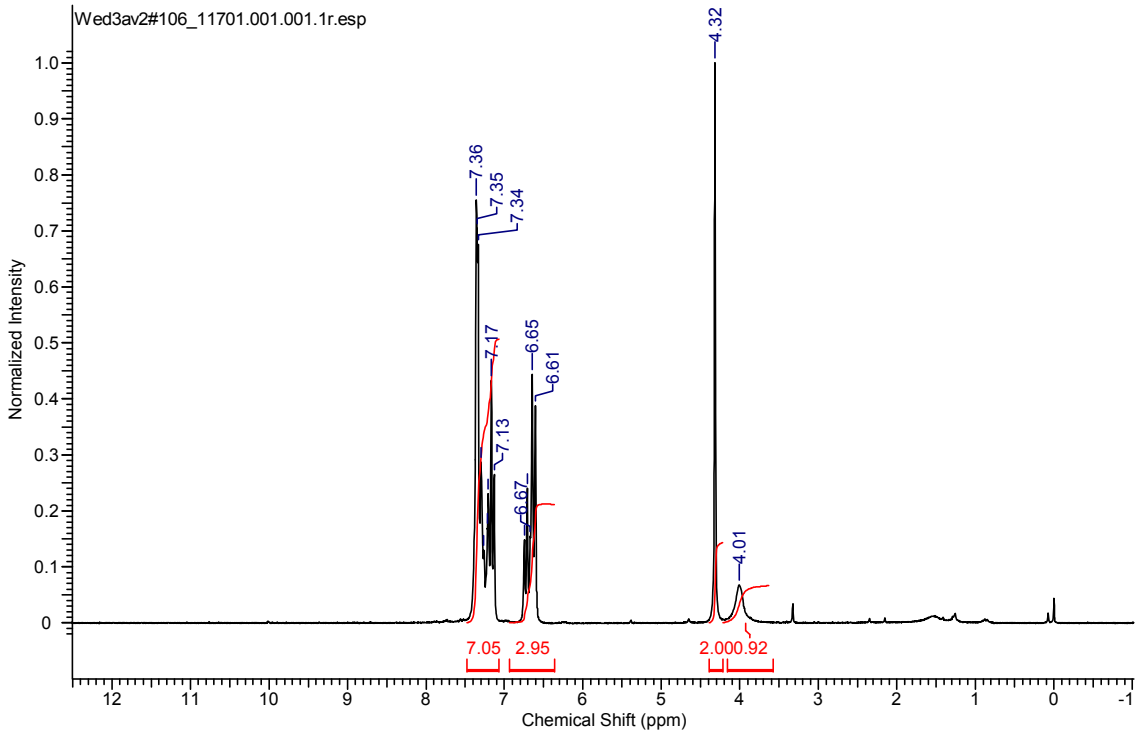
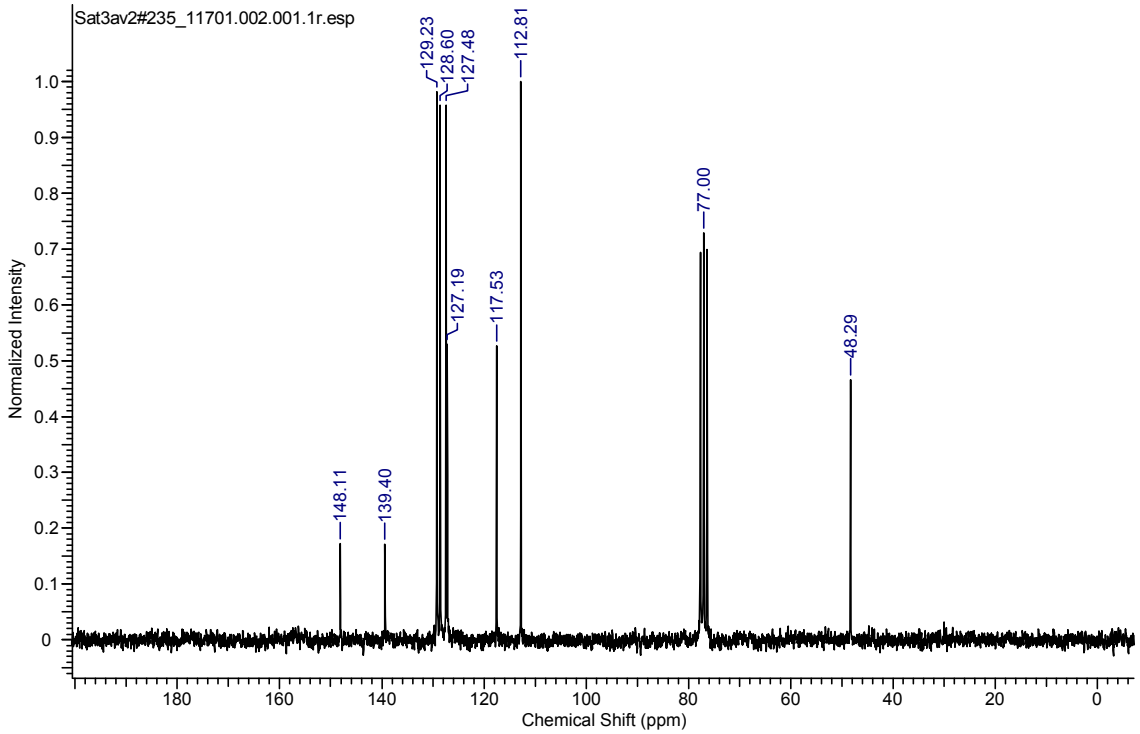
^{1}H NMR Spectrum of Isolated **N-benzylaniline (16)** ($CDCl_3$, 200 MHz, 298 K)



^{13}C NMR spectrum of Isolated **N-benzylaniline (16)** ($CDCl_3$, 50.28 MHz, 298 K)



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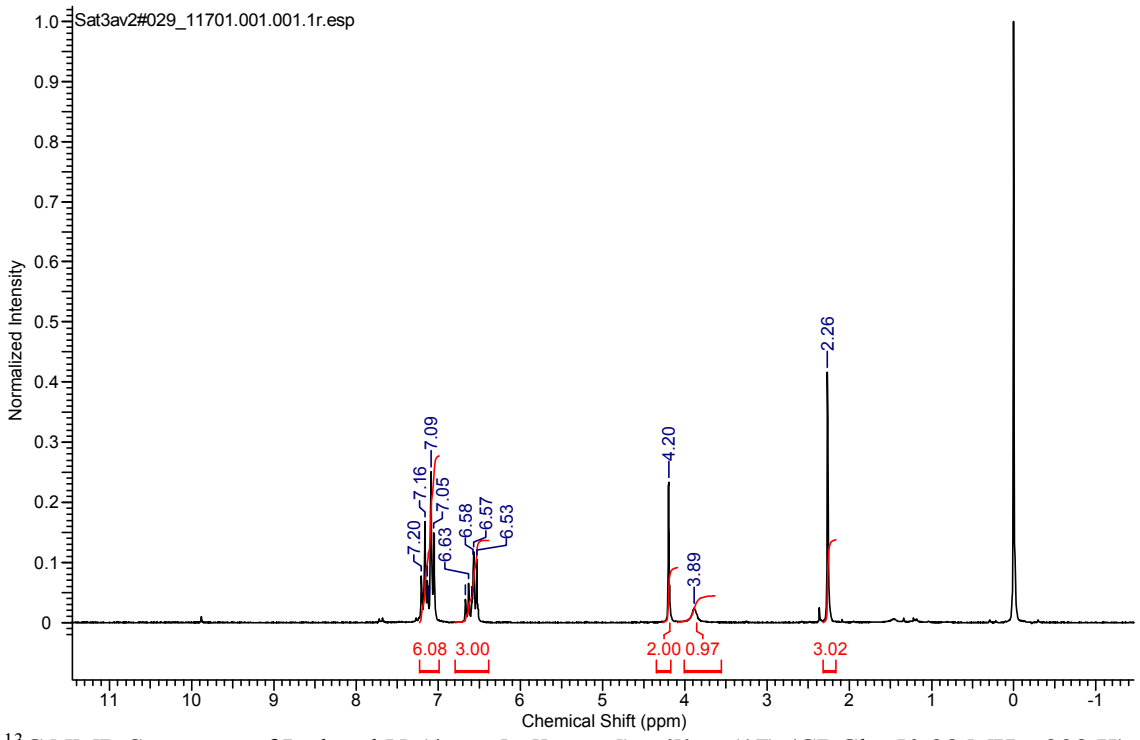
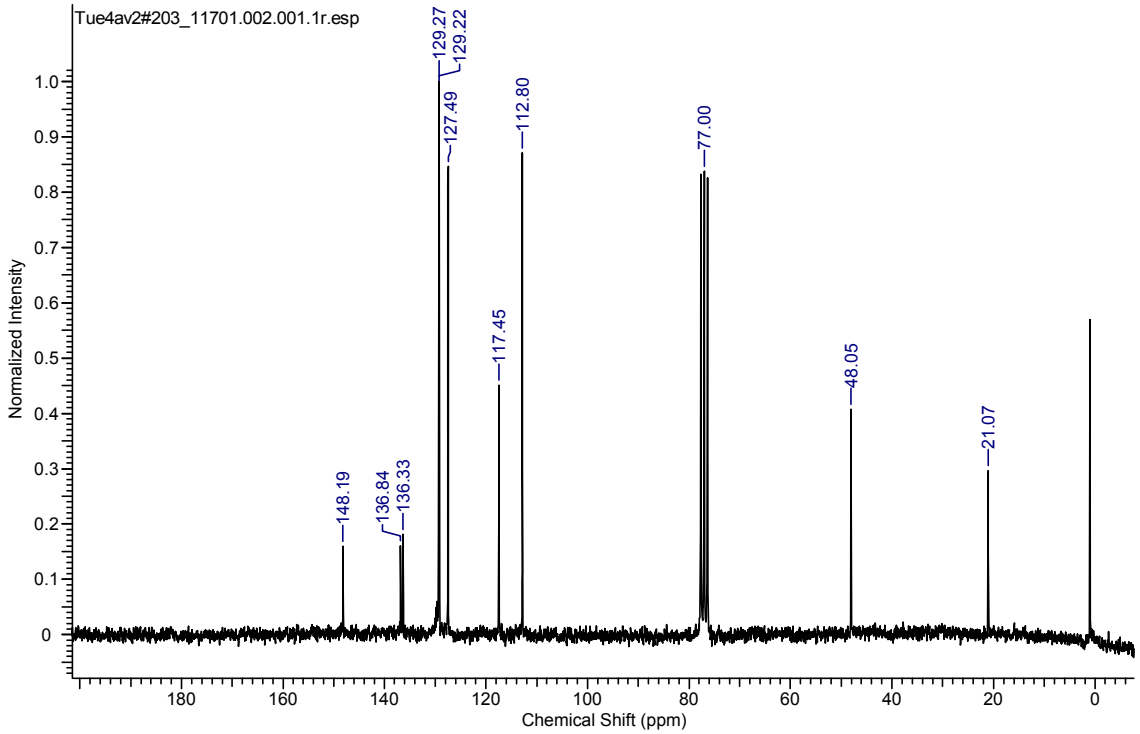
^{1}H NMR Spectrum of Isolated **N-(4-methylbenzyl)aniline (17)** ($CDCl_3$, 200 MHz, 298 K)



^{13}C NMR Spectrum of Isolated **N-(4-methylbenzyl)aniline (17)** ($CDCl_3$, 50.28 MHz, 298 K)



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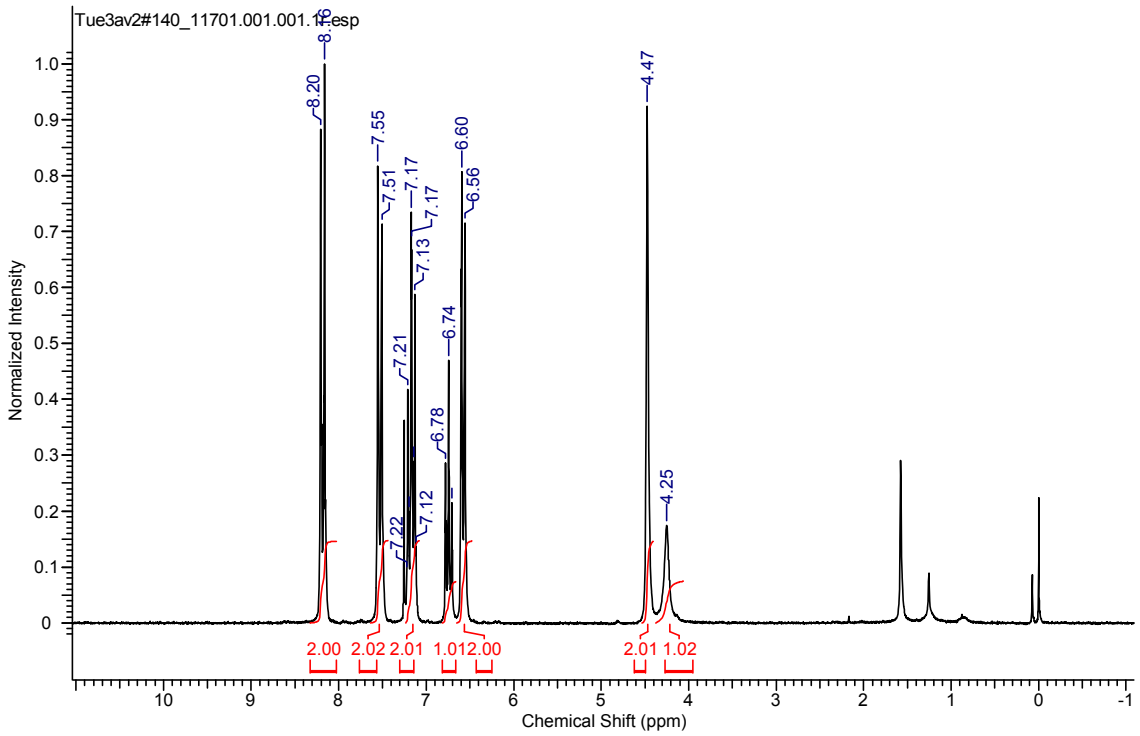
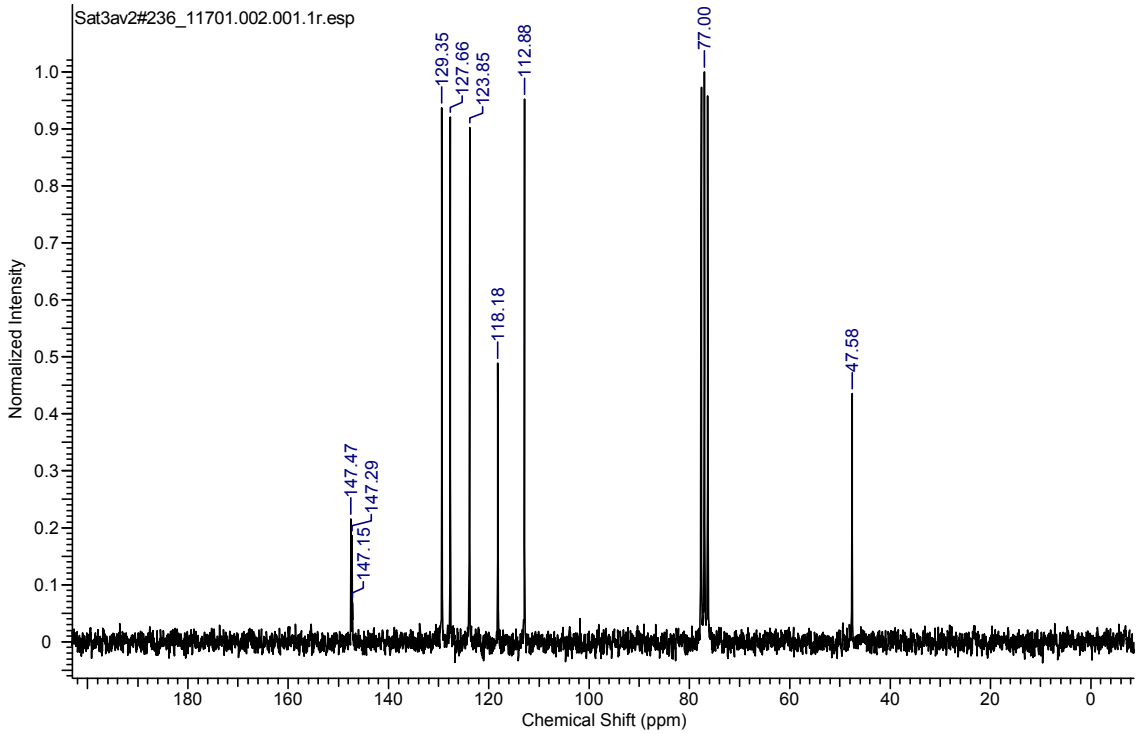
^{1}H NMR Spectrum of Isolated **N-(4-nitrobenzyl)aniline (18)** ($CDCl_3$, 200 MHz, 298 K)



^{13}CNMR Spectrum of Isolated **N-(4-nitrobenzyl)aniline (18)** ($CDCl_3$, 50.28 MHz, 298 K)



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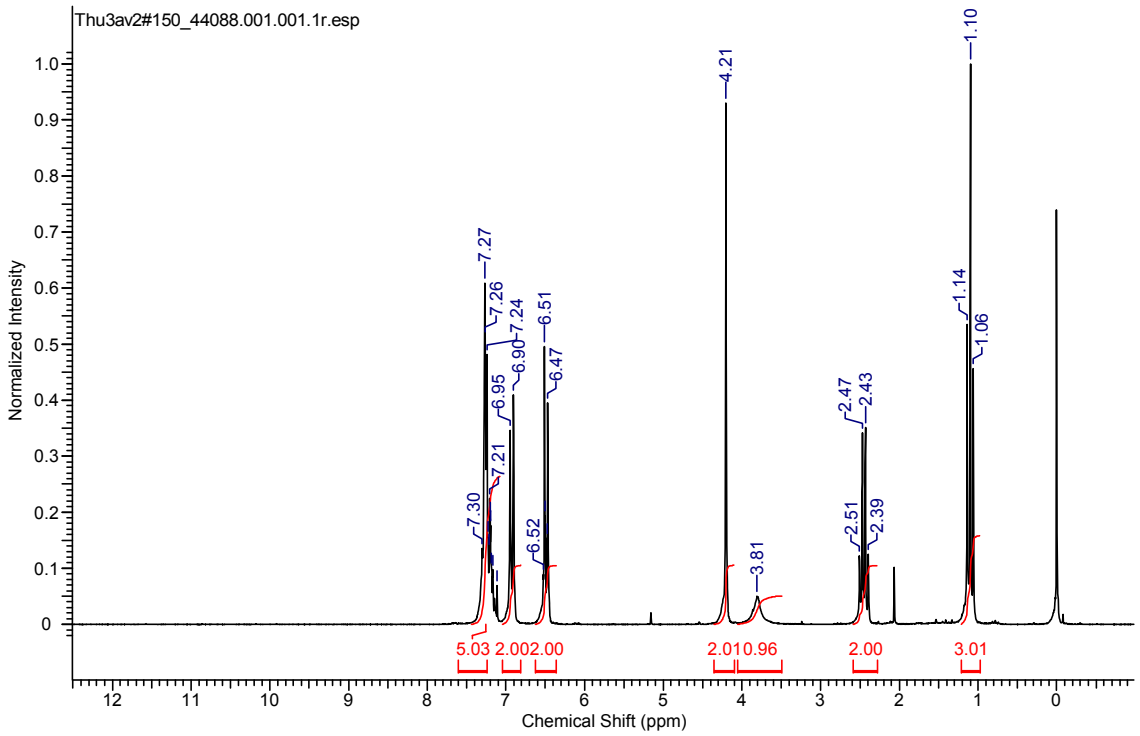
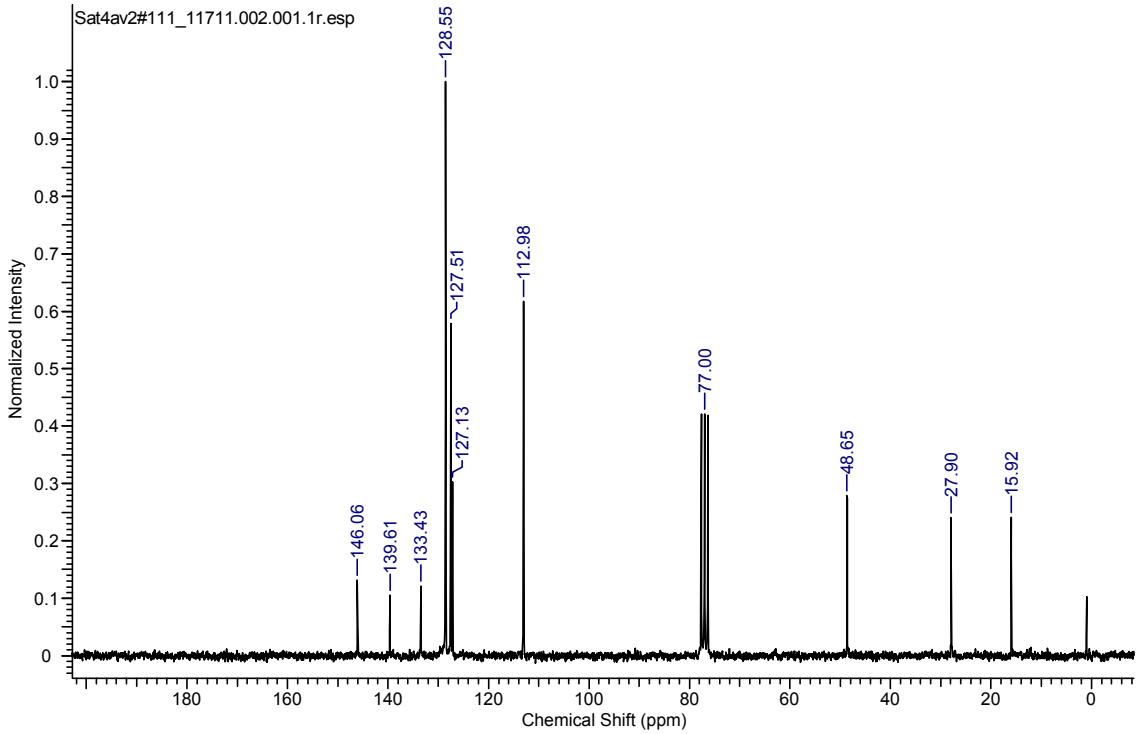
^{1}H NMR Spectrum of Isolated **N-benzyl-4-ethylaniline (19)** ($CDCl_3$, 200 MHz, 298 K)



^{13}C NMR Spectrum of Isolated **N-benzyl-4-ethylaniline (19)** ($CDCl_3$, 50.28 MHz, 298 K)



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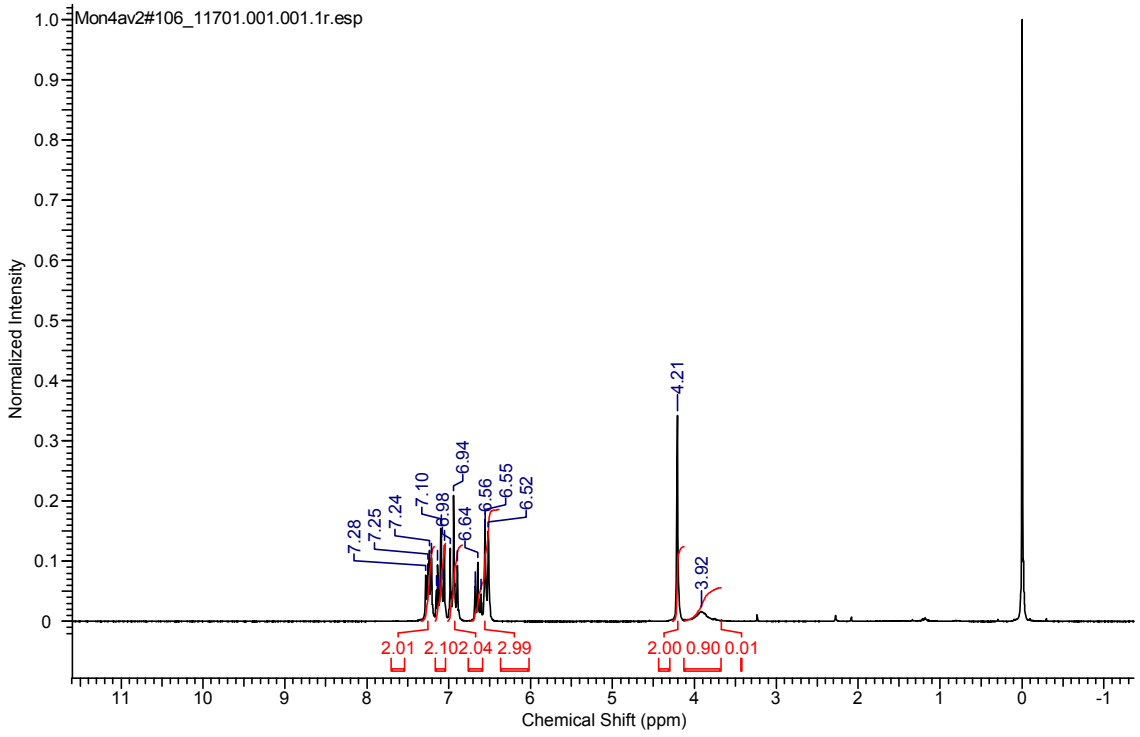
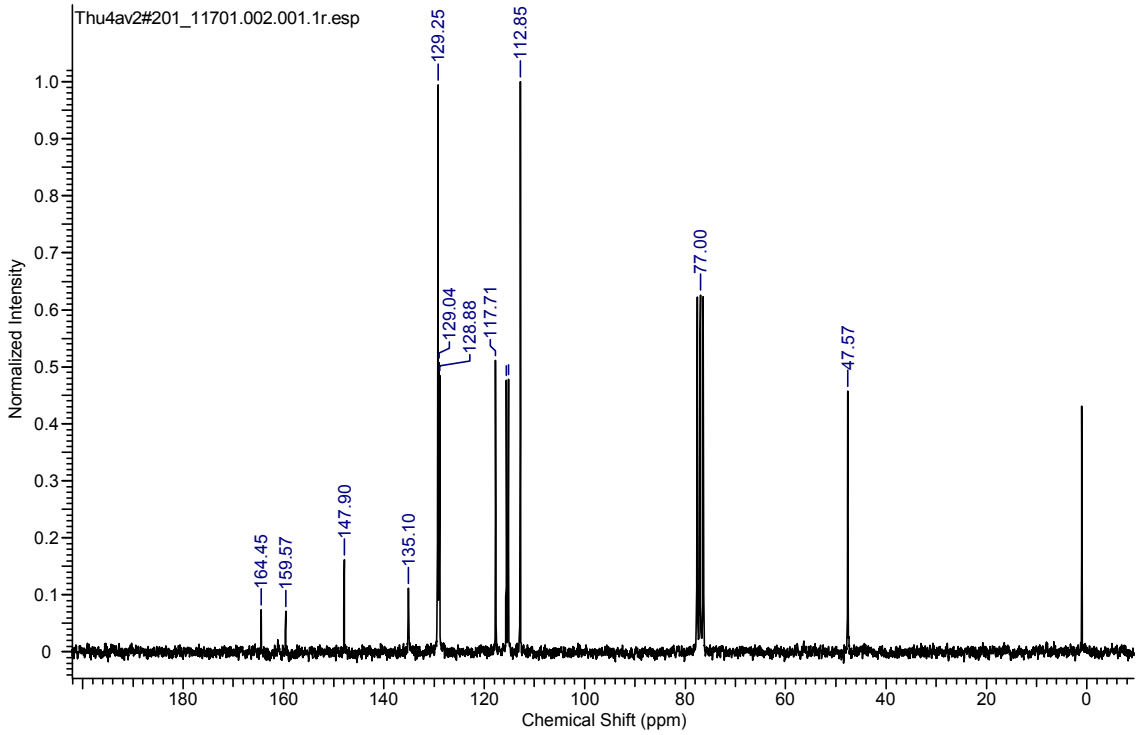
^{1}H NMR Spectrum of Isolated **N-(4-fluorobenzyl)aniline (20)** ($CDCl_3$, 200 MHz, 298 K)



^{13}C NMR Spectrum of Isolated **N-(4-fluorobenzyl)aniline (20)** ($CDCl_3$, 50.28 MHz, 298 K)



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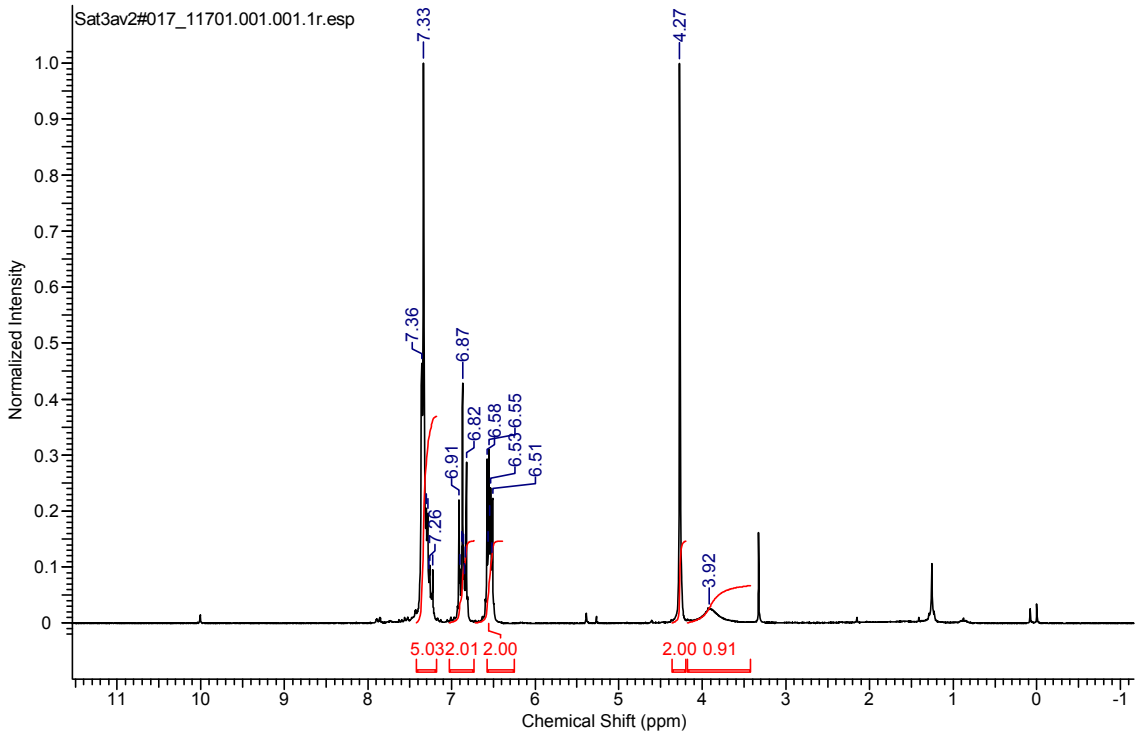
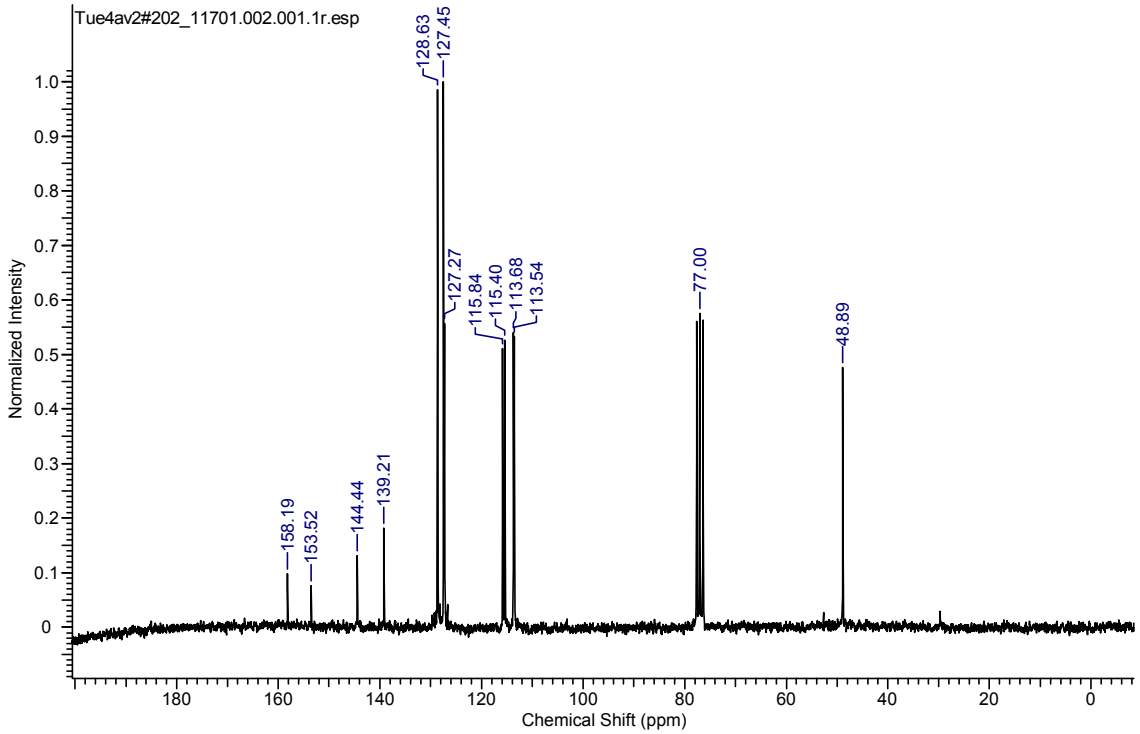
^{1}H NMR Spectrum of Isolated **N-benzyl-4-fluoroaniline (21)** ($CDCl_3$, 200 MHz, 298 K)



^{13}C NMR Spectrum of Isolated **N-benzyl-4-fluoroaniline (21)** ($CDCl_3$, 50.28 MHz, 298 K)



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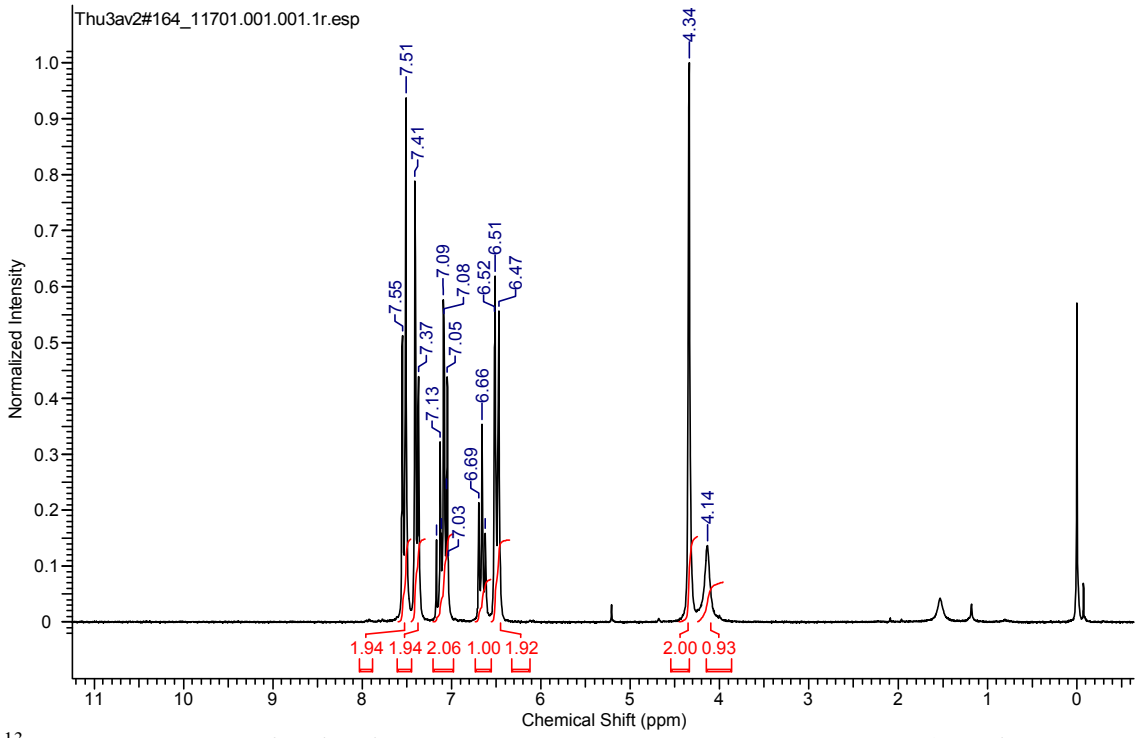
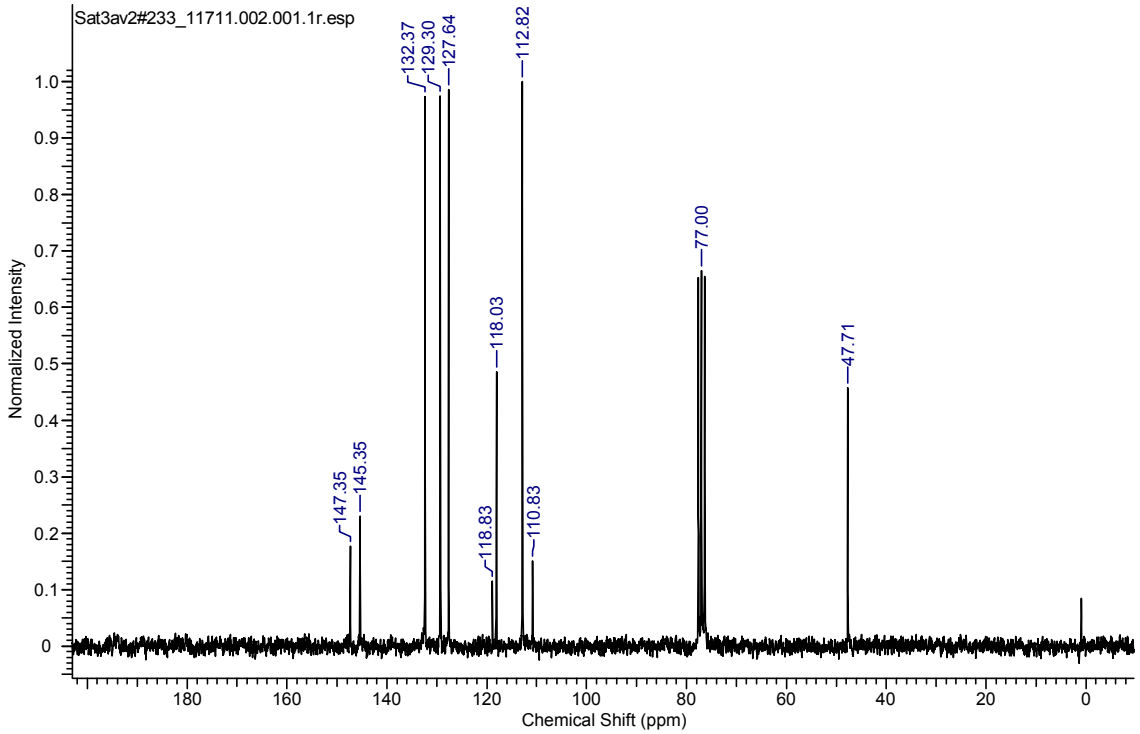
^{1}H NMR Spectrum of Isolated **4-((phenylamino)methyl)benzonitrile (22)** ($CDCl_3$, 200 MHz, 298 K)



^{13}C NMR Spectrum of Isolated **4-((phenylamino)methyl)benzonitrile (22)** ($CDCl_3$, 50.28 MHz, 298 K)



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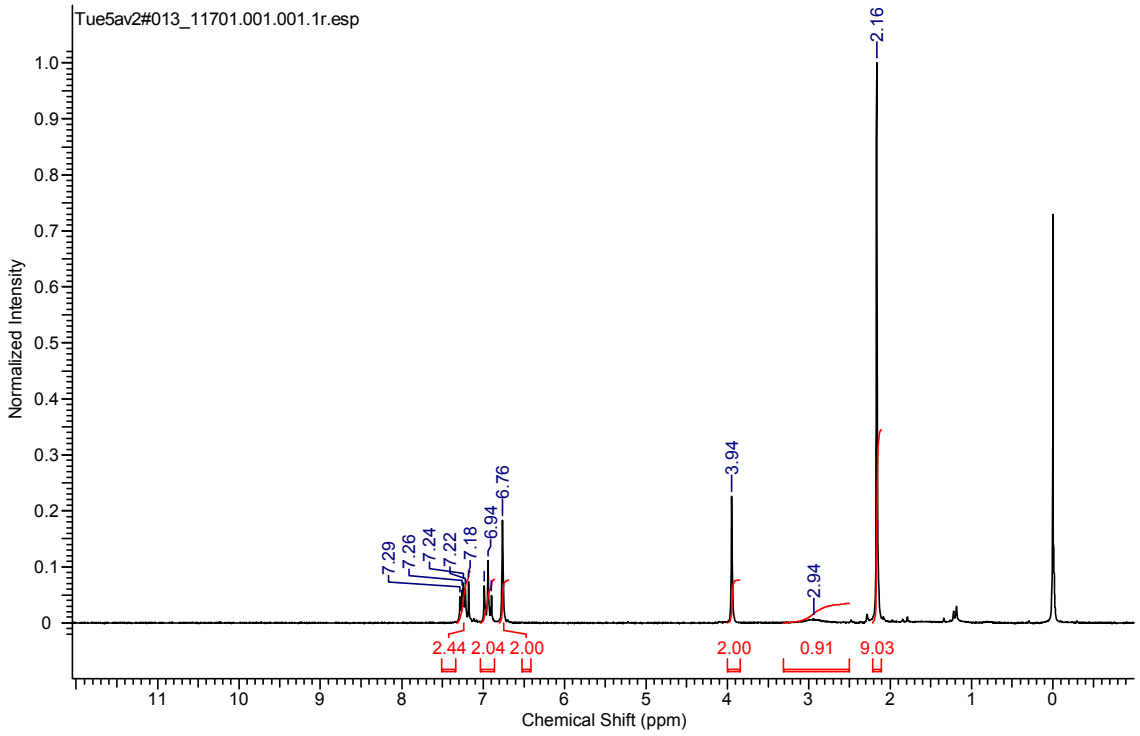
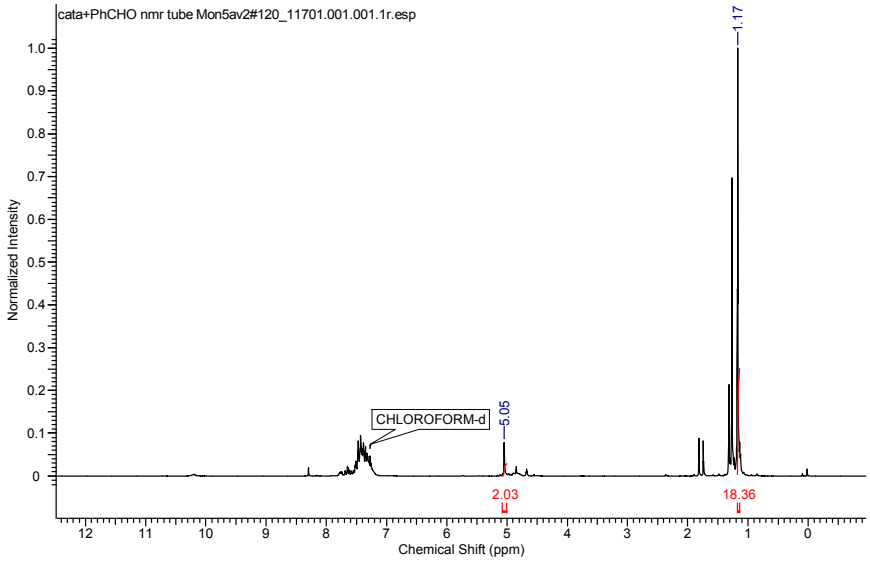
^{1}H NMR Spectrum of isolated **N-(4-fluorobenzyl)-2,4,6-trimethylaniline (23)** ($CDCl_3$, 200 MHz, 298 K)



^{1}H NMR Spectrum of **Int-2** ($CDCl_3$, 200 MHz, 298 K)



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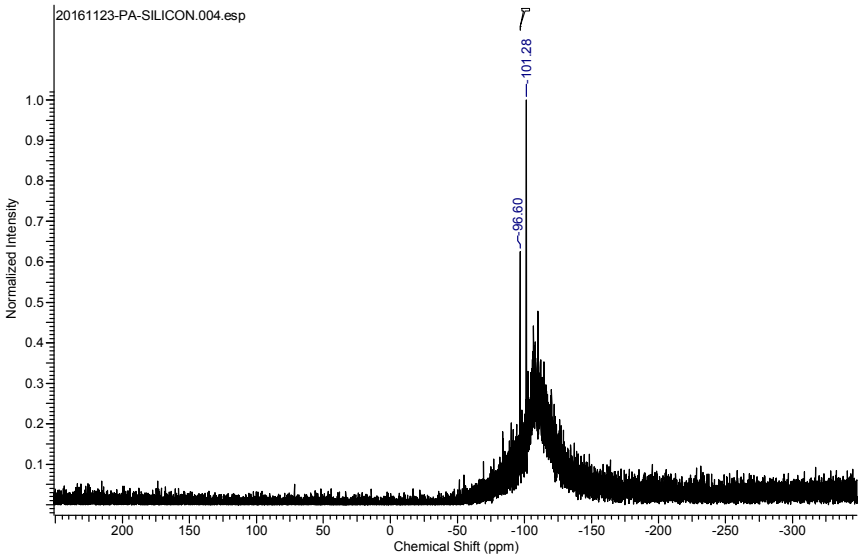
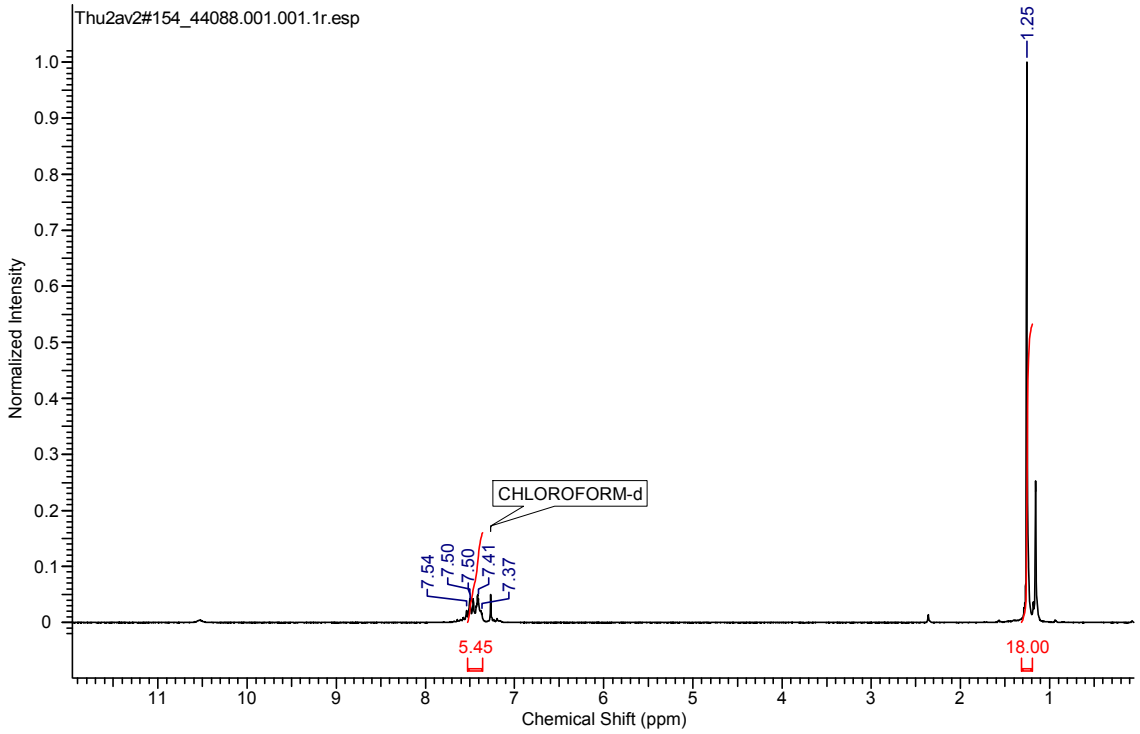
$^{29}Si\{^{1}H\}$ NMR Spectrum of **Int-2** ($CDCl_3$, 200 MHz, 298 K)



^{1}H NMR of $PhC(NtBu)_2SiCl_3$ ($CDCl_3$, 200MHz, 298K):



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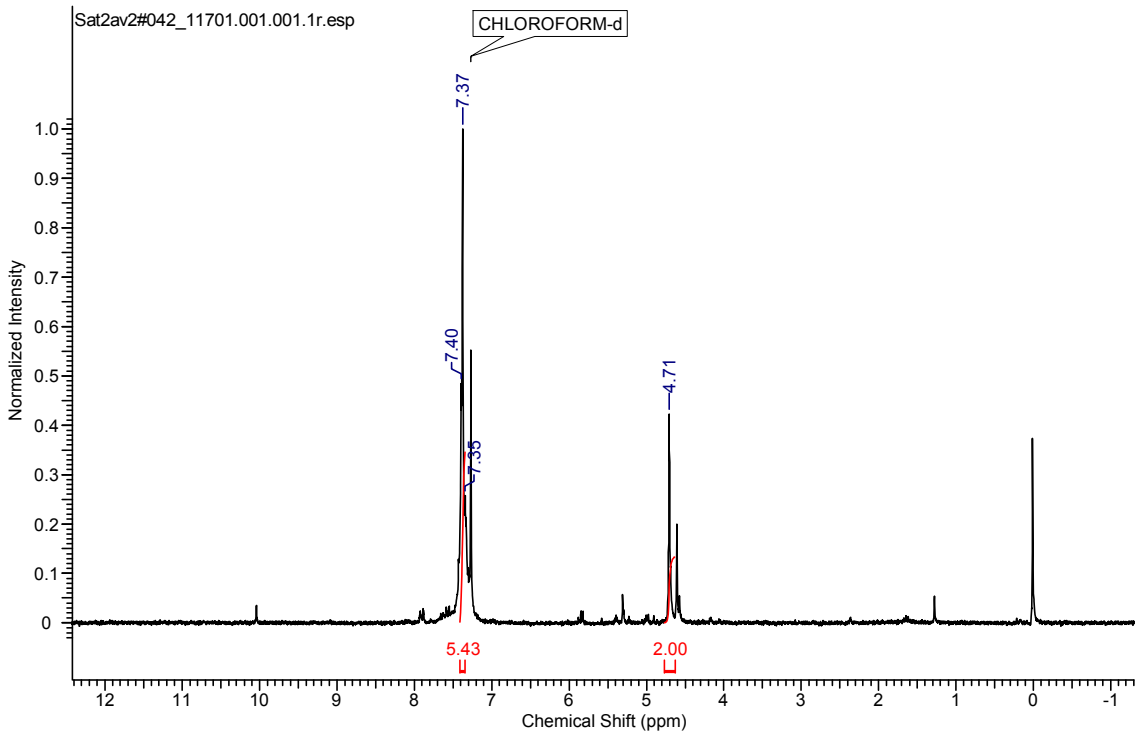
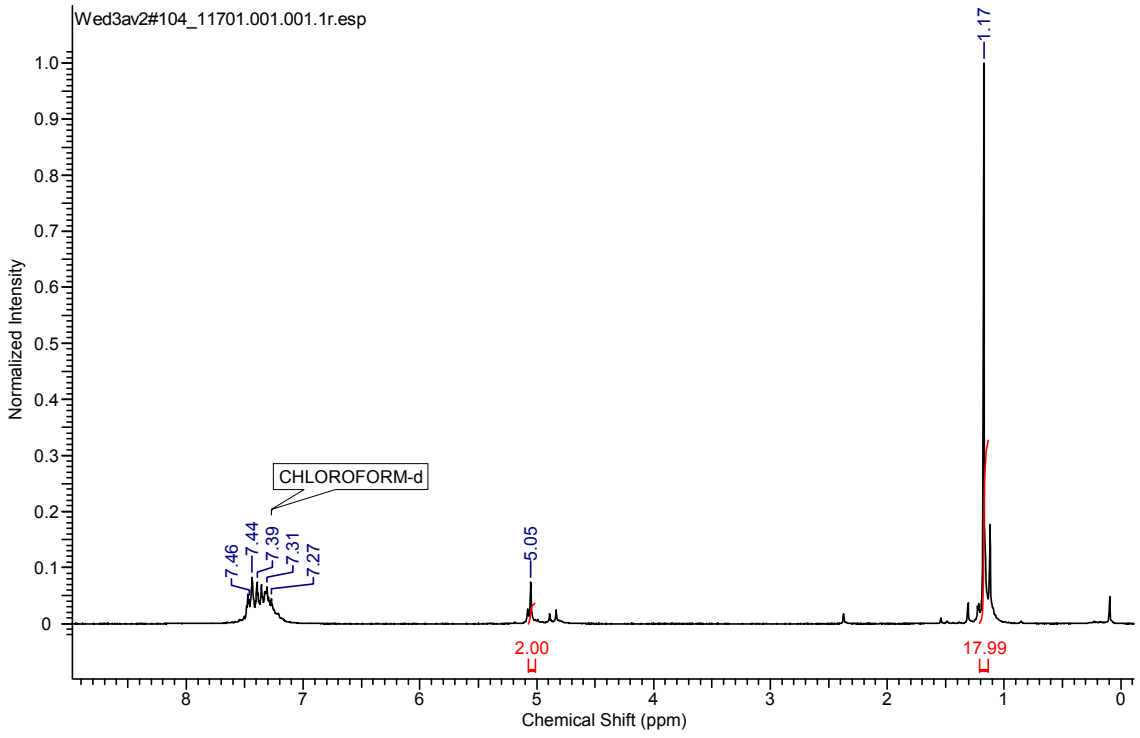
^{1}H NMR of BnOK($CDCl_3$, 200MHz, 298K):



^{1}H NMR of **Int-2** ($CDCl_3$, 200 MHz, 298K):



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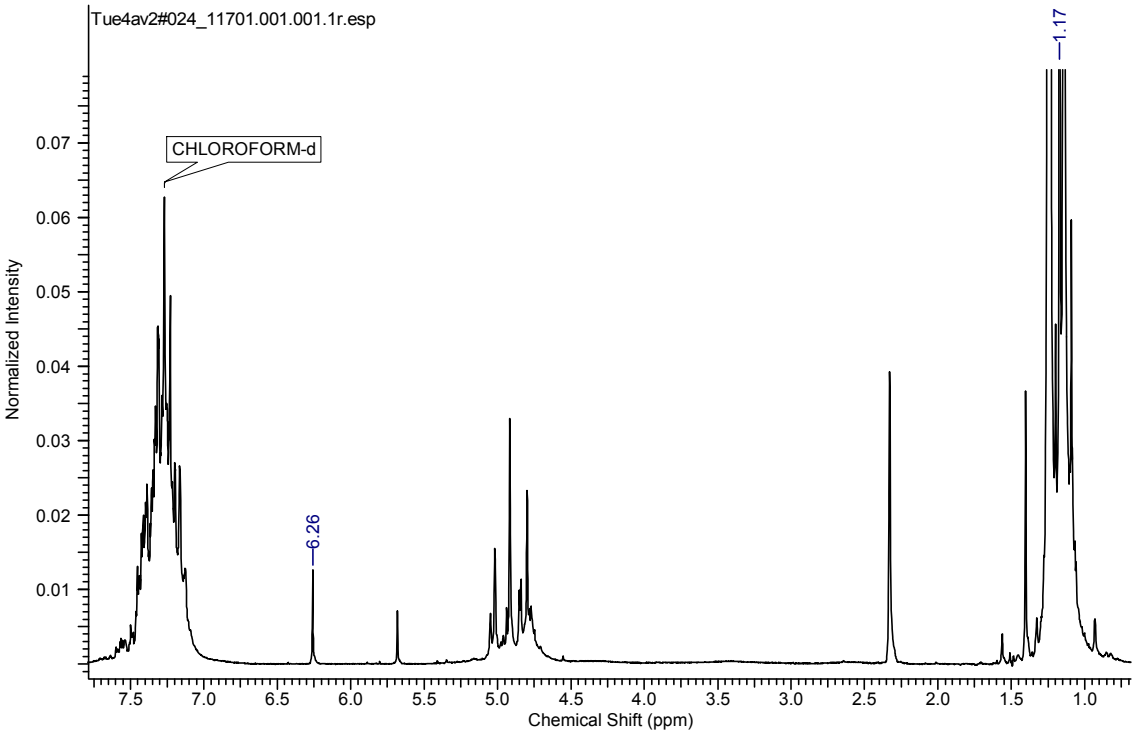
^{1}H NMR of the reaction of **Int-2** with HBpin ($CDCl_3$, 200MHz, 298K):



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