Supplementary Information

for

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

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Contents:

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%**)**,^1H 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 $PhC(NtBu)_2SiCl_3$ (0.5 g, 1.36 mmol) was added drop by drop at -78 °C. The reaction mixture was stirred for 30 min at -78 °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

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.

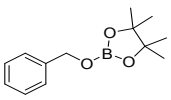
Upon completion of the reaction, three of the resulted boronate ester residue were hydrolysed by silica gel with methanol at 60 °C for 4–6 hrs. The completion of hydrolysis was checked by TLC. Upon completion, the reaction mixture was filtered and washed three times with dichloromethane. The combined 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

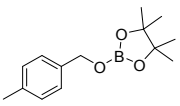
entry	catalyst (mol%)	temp.	Time (h)	Conv. (%)
1	**0.5**	**rt**	**1**	**77**
2	**0.5**	**50 °C**	**1**	**88**
3	**1.0**	**rt**	**1**	**96**
4	**1.5**	**rt**	**1**	**96**

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

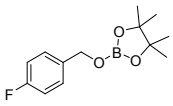
2-(benzyloxy)-pinacolborane (2): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.28-7.18 (m, 5H, Ar*H*), 4.85 (s, 2H, OCH_2), 1.18 (s, 12H, CH_3) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.48 (*C*H_3), 66.55 (*C*H_2), 82.90 (*C*$(CH_3)_2$), 126.65 (*Ph*), 127.27 (*Ph*), 128.20 (*Ph*), 139.16 (Ar*C*-R)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

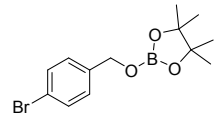


2-((4-fluorobenzyl)oxy)-pinacolborane (4): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.30-



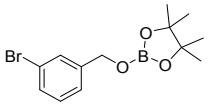
6.85 (m, 4H, Ar*H*), 4.80 (s, 2H, CH_2), 1.19 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.51 (*C*H_3), 65.98 (*C*H_2), 83.01 (*C*$(CH_3)_2$), 115.05 (d, $J_{C\text{-}F}$=21.22 Hz, Ar-*C*), 128.58 (d, $J_{C–F}$=8.05 Hz, Ar-*C*), 134.88 (Ar-C), 162.13 (*d*, $J_{C\text{-}F}$ = 245.17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

2-((4-bromobenzyl)oxy)-pinacolborane (5): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.36 (d,



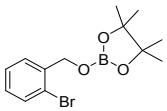
2H, Ar*H*), 7.12(d, 2H, Ar*H*), 4.78 (s, 2H, CH_2), 1.18 (s, 12H, CH_3) ppm.

2-((3-bromobenzyl)oxy)-pinacolborane (6): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.49-



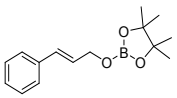
7.06 (m, 4H, Ar*H*), 4.81 (s, 2H, CH_2), 1.19 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.56 (*C*H_3), 65.77 (*C*H_2), 83.12 (*C*$(CH_3)_2$), 125.09 (*Ph*), 129.66 (*Ph*), 129.81 (*Ph*), 130.37 (*Ph*), 137.24 (*Ph*), 141.45 (*Ph*) ppm.

2-((2-bromobenzyl)oxy)-pinacolborane (7): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.47-



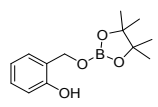
6.97(m, 4H, Ar*H*), 4.90(s, 2H, CH_2), 1.19 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.53 (*C*H_3), 66.21 (*C*H_2), 83.08 (*C*$(CH_3)_2$), 121.45 (*Ph*), 127.27 (*Ph*), 127.73 (*Ph*), 128.54 (*Ph*), 132.18 (*Ph*),138.25 (*Ph*) ppm.

2-(cinnamyloxy)-pinacolborane (8): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.32-7.09 (m,



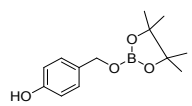
5H, Ar*H*), 6.61-6.49 (d, 1H, $^{3}J_{H\text{-}H}$=15.7 Hz, 1H ArC*H*), 6.29-6.13 (m, 1H, CHC*H*), 4.48-4.45 (d, 2H, $^{3}J_{H\text{-}H}$=5.3 Hz, CH_2), 1.18 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 24.51 (*C*H_3), 65.17 (*C*H_2), 82.87 (*C*$(CH_3)_2$), 126.34 (*Ph*), 126.69 (*Ph*),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

($CDCl_3$, 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, C*H*$_2$), 3.71 (s, 3H, OC*H*$_3$), 1.18 (s, 12H, C*H*$_3$) 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, C*H*$_2$), 3.70 (s, 3H, OC*H*$_3$), 1.18 (s, 12H, C*H*$_3$) 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, C*H*$_2$), 1.19 (s, 12H, C*H*$_3$) 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, C*H*$_2$), 1.19 (s,12H, C*H*$_3$) ppm.

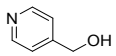
2-isobutoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 3.60 (d, $^3J_{H\text{-}H}$=6.57 Hz, 2H, C*H*$_2$), 1.81 (sept, 1H, C*H*$(CH_3)_2$) , 1.25 (s, 12H, C*H*$_3$), 0.88 (d, $^3J_{H\text{-}H}$=6.69 Hz, 6H, CH(C*H*$_3$)$_2$) ppm; ^{13}C NMR ($CDCl_3$, 50.28 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:

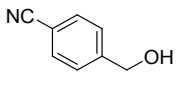
4-bromo benzyl alcohol (5'): Yield: 146.5 mg (78.3%); ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.42-7.37 (d, $^3J_{H\text{-}H}$=8.46 Hz, 2H, Ar*H*), 7.17-7.13 (d, ^3J=7.83 Hz, 2H, Ar*H*), 4.55 (s, 2H, C*H*$_2$), 1.61 (s, 1H, O*H*) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 64.58 (CH_2), 128.32 (*Ph*), 128.57 (*Ph*), 139.74 (*Ph*) ppm.

(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

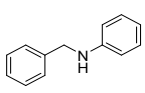
Imine (1 mmol), pinacolborane (1 mmol), catalyst **1**(2 mol %), acetonitrile (1 mL) were charged in a Schlenk tube with a magnetic bead inside the glove box. The reaction mixture was allowed to stir at room temperature and then slowly heated at 65 ^{o}C for 48-72 h. The progress of the reaction was 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, 129.23, 128.60, 127.48, 127.19, 117.53, 112.81 (*Ph*), 48.29 (CH_2) ppm.

N-(4-methylbenzyl)aniline (17): Isolated Yield: 146 mg (74%); ^1H 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 (CH_2), 21.07 (CH_3) ppm.

N-(4-nitrobenzyl)aniline (18): Isolated Yield: 198.5 mg (87%); ^1H 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;$^{13}C\{^1H\}$ 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 (CH_2) ppm.

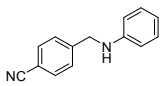
N-benzyl-4-ethylaniline (19): Isolated Yield: 186 mg (88%); ^1H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.31-7.11 (m, 5H, Ar*H*), 6.95-6.90 (d, $^3J_{H-H}$ =8.46 Hz, 2H,Ar*H*), 6.51-6.47 (d, $^3J_{H-H}$ =6.46 Hz, 2H, Ar*H*), 4.21 (s, 2H, CH_2), 3.81 (s, 1H,N*H*), 2.51-2.39 (q, $^3J_{H-H}$ =22.74 Hz, 2H, CH_2CH_3),1.14-1.06 (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 (CH_2NH), 27.90 (CH_2CH_3), 15.92 (CH_2CH_3) ppm.

N-(4-fluorobenzyl)aniline (20): Isolated Yield: 152.9 mg (76%); ^1H 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 (CH_2) ppm.

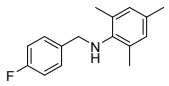
N-benzyl-4-fluoroaniline (21): Isolated Yield: 158.9 mg (79%); ^1H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.36-7.23 (m, 5H, Ar*H*), 6.91-6.82 (m, 2H, Ar*H*), 6.58-6.51 (m, 2H, Ar*H*), 4.27 (s, 2H, CH_2), 3.92 (s, 1H, N*H*) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 155.85 (d, J_{C-F}=234.92 Hz, 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 (*C*H_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 (*C*H_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

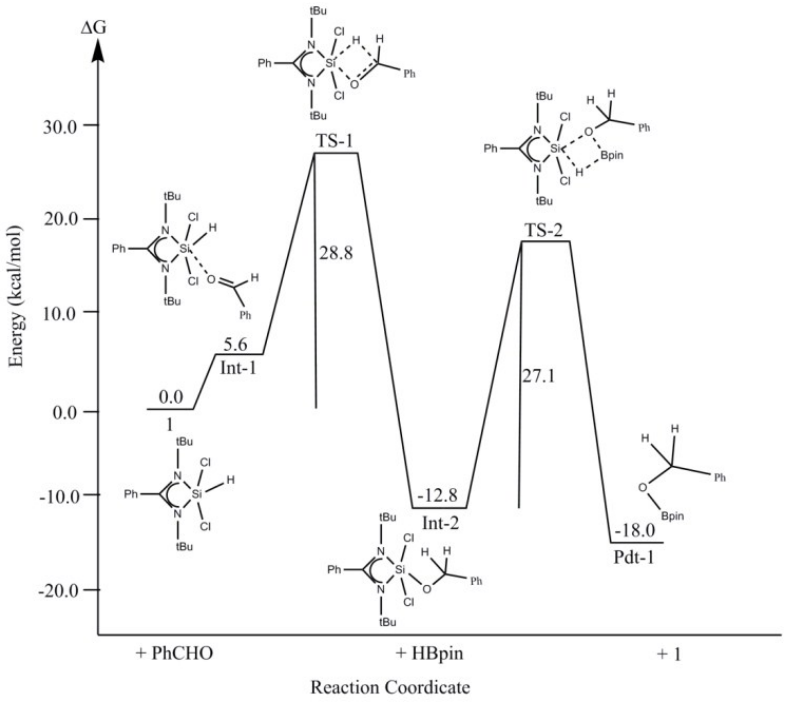
All the calculations in this study have been performed with density functional theory (DFT), with the aid of the Turbomole 6.4 suite of programs,[S3] using the PBE functional.[S4] The TZVP[S5] basis set has been employed. The resolution of identity (RI),[S6] along with the multiple accelerated resolution 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 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.

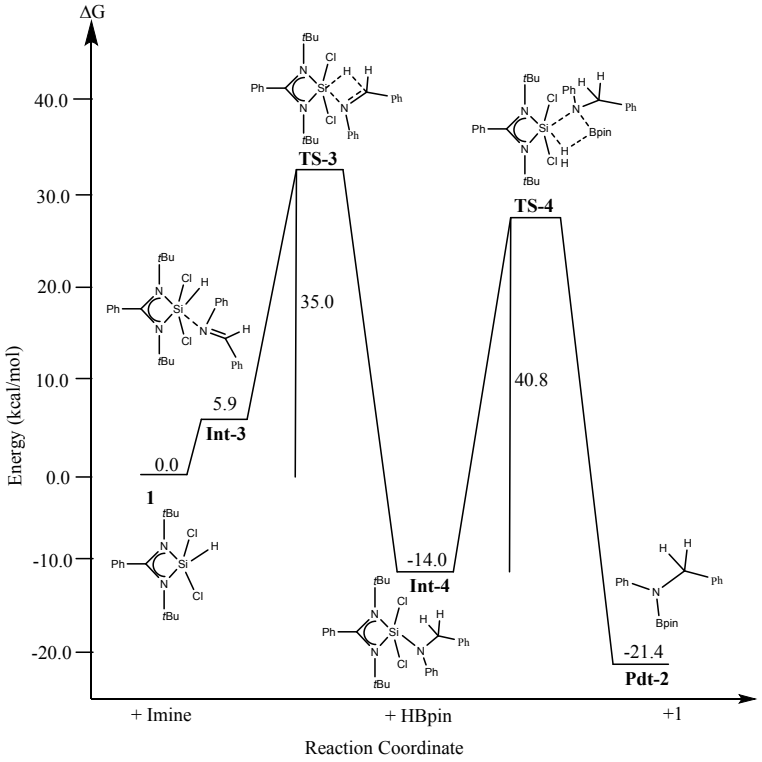


Figure S1. The reaction energy profile diagram for the catalytic imine hydroboration by catalyst **1**. The values (in kcal/mol) have been calculated at the PBE/TZVP level of theory with DFT.

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

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

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

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

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

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

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

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

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

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

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

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

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
C	-2.688636	-5.247930	-3.947199
C	-0.360474	-6.192167	-2.456064
H	-1.808399	1.953747	1.161884
H	1.622419	3.340348	-1.052779
H	-2.225958	4.274094	1.968418
H	1.384897	-1.126589	2.450663
H	3.066789	-0.645045	2.741159
H	2.668364	-1.609681	1.304202
H	1.203686	5.660055	-0.259388
H	-0.718267	6.130581	1.260593
H	-3.066276	0.776773	-1.322500
H	-3.292971	1.864351	-2.716527
H	-2.470792	2.455809	-1.259514
H	-0.480151	3.175343	-2.546642
H	-1.236344	2.642626	-4.059343
H	0.385115	2.038535	-3.619042
H	1.611793	2.569397	1.855955
H	2.303337	1.501028	3.088207
H	0.608736	1.293807	2.593790
H	3.821084	0.236314	-0.130088
H	4.191800	1.116334	1.380094

H	3.317682	1.935595	0.059142
H	-0.639718	-0.246005	-4.107774
H	-2.241789	0.485982	-4.340010
H	-2.036127	-0.831422	-3.168084
H	0.821749	-2.978868	1.039510
H	0.151277	-4.219072	2.798735
H	-2.241756	-4.347754	-0.775513
H	-3.859269	-5.845955	0.353422
H	-3.484819	-6.540025	2.723168
H	-1.464717	-5.716708	3.941201
H	0.754224	-4.001635	-0.395159
H	0.281758	-1.854791	-2.946446
H	-0.345576	-3.327079	-5.645140
H	-1.222059	-4.759043	-6.252578
H	-2.118995	-3.294591	-5.770100
H	0.209295	-6.552517	-5.185721
H	1.118431	-5.025379	-5.356170
H	1.646495	-6.252546	-4.180300
H	-3.537822	-4.656499	-4.317865
H	-2.630813	-6.171194	-4.541608
H	0.603281	-6.505627	-2.030959
H	-2.883597	-5.516965	-2.901617
H	-0.860127	-7.080715	-2.867285
H	-0.975082	-5.791150	-1.643104
H	-0.610453	-1.049244	1.808779
H	-2.810036	-2.219536	-1.691640
H	-2.688840	-0.194819	2.847997
H	-4.908914	-1.375874	-0.658443
H	-4.860114	-0.352435	1.619967

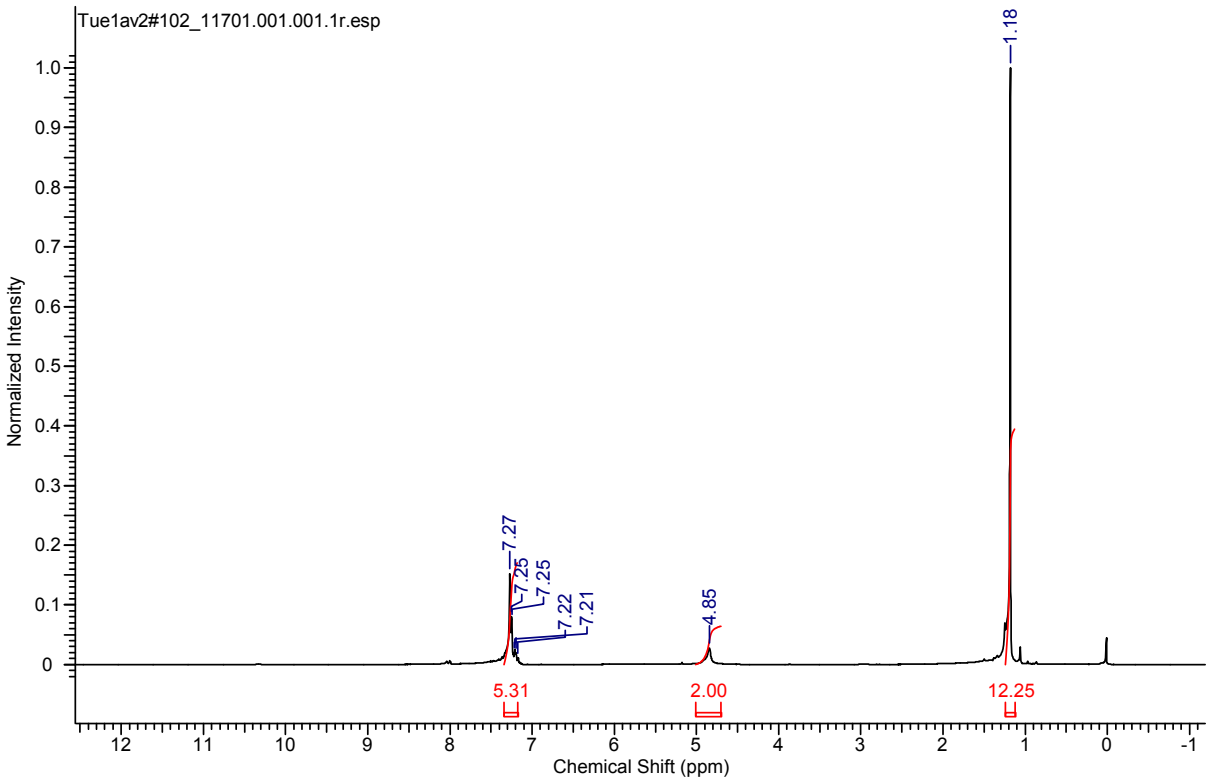
Pdt-2
PBE/TZVP Energy : -1802309.46 kcal/mol

C	-1.058642	3.608424	1.253971
C	-0.622634	3.905925	-0.045045
C	-0.771133	5.201035	-0.558696
C	-1.351408	6.196928	0.230360
C	-1.796336	5.899479	1.523375
C	-1.652366	4.603309	2.031396
C	-0.060395	2.810936	-0.871297
N	1.143817	2.183576	-0.668636
C	2.367329	2.646914	0.062519
C	2.639139	1.681544	1.227836
N	-0.674882	2.179239	-1.852804
C	-2.044469	2.291417	-2.406199
C	-3.106539	2.682179	-1.364432
Si	0.759932	0.823348	-1.851358
Cl	2.471691	-0.558495	-1.492581
N	-0.019623	-1.847002	1.111453
B	-0.246105	-2.724121	-0.013074
O	-1.385988	-2.765848	-0.803894
C	-1.088954	-3.680378	-1.920913
C	-2.368755	-4.417849	-2.286478
C	1.268941	-2.010670	1.795308
C	1.231296	-2.843229	3.065816

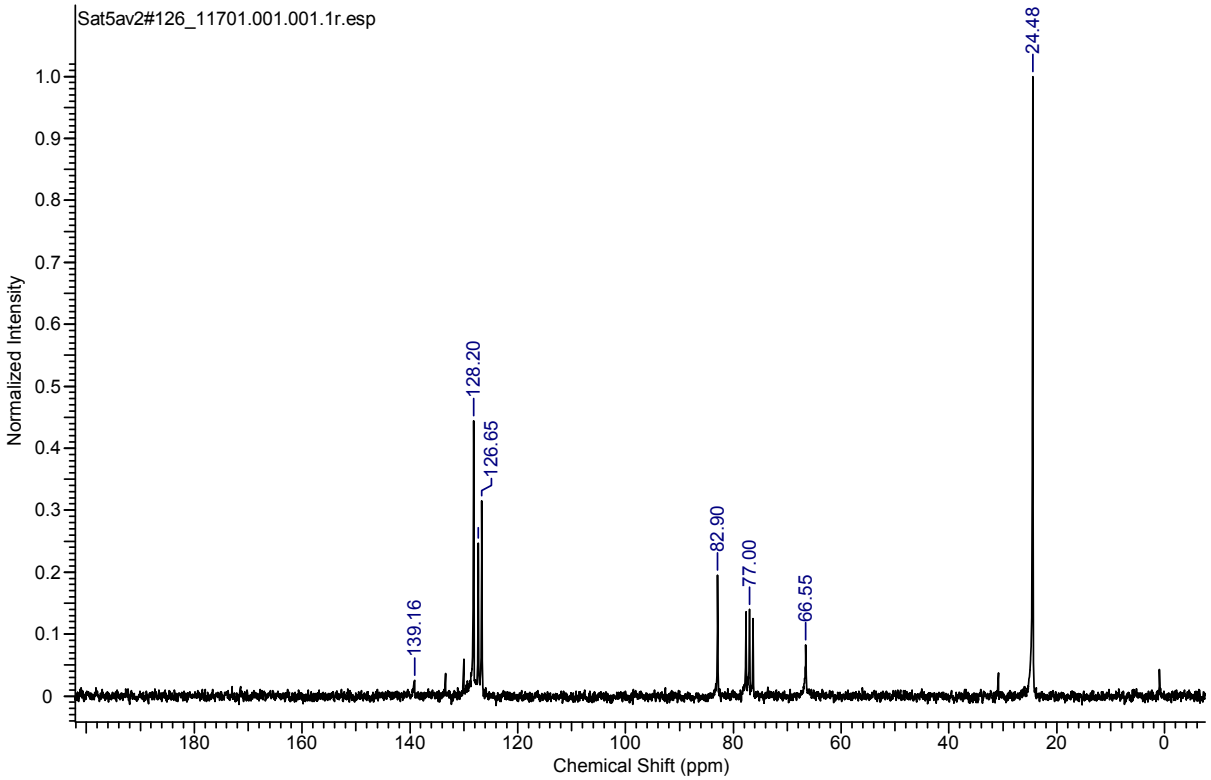
C	2.230684	-2.667397	4.035018
C	2.249525	-3.450077	5.193416
C	1.261160	-4.419288	5.401204
C	0.258735	-4.597475	4.441517
C	0.245735	-3.815112	3.282330
C	-0.943442	-0.932294	1.659172
C	-2.177235	-0.655308	1.026704
C	-3.094514	0.223040	1.602714
C	-2.820246	0.869238	2.813078
C	-1.596323	0.617578	3.437070
C	-0.671081	-0.267083	2.876237
Cl	1.217572	1.109366	-3.919067
C	-2.013844	3.320464	-3.552529
C	-2.410483	0.908361	-2.976604
C	2.236004	4.071848	0.623969
C	3.541938	2.663251	-0.934772
O	0.702807	-3.673500	-0.371168
C	0.047562	-4.584993	-1.315941
C	-0.493660	-5.758229	-0.494920
C	1.082613	-5.064440	-2.323199
C	-0.607776	-2.822272	-3.091910
H	-0.954490	2.594018	1.643682
H	-0.422258	5.432306	-1.566600
H	-2.003597	4.364350	3.037223
H	1.785643	1.674673	1.922125
H	3.535569	2.000780	1.779674
H	2.801066	0.661079	0.861162
H	-1.459283	7.207637	-0.167500
H	-2.256747	6.677990	2.134653
H	-3.050662	2.026895	-0.484707
H	-4.101073	2.567335	-1.819786
H	-3.007039	3.721703	-1.031190
H	-1.771043	4.322050	-3.170799
H	-2.998466	3.367821	-4.040973
H	-1.261083	3.039059	-4.301789
H	1.993510	4.802222	-0.159321
H	3.212622	4.345113	1.047937
H	1.489746	4.150588	1.422636
H	3.724516	1.673195	-1.367307
H	4.456868	2.985555	-0.416702
H	3.337529	3.372983	-1.749857
H	-1.670024	0.575170	-3.717221
H	-3.388915	0.967168	-3.473212
H	-2.473046	0.154411	-2.178938
H	1.693920	-1.018859	2.012194
H	3.000468	-1.905430	3.881756
H	-0.544305	-3.954177	2.541449
H	-0.519086	-5.348510	4.596504
H	1.270094	-5.028217	6.307524
H	3.033651	-3.298337	5.938412
H	1.957979	-2.480867	1.081231
H	-0.209199	-0.243447	-1.493927
H	0.326920	-2.298800	-2.846814
H	-0.443832	-3.435560	-3.988719
H	-1.374582	-2.070610	-3.322135

H	0.605208	-5.672698	-3.105415
H	1.599245	-4.221358	-2.797254
H	1.831371	-5.688955	-1.815288
H	-3.101446	-3.706368	-2.693277
H	-2.165768	-5.175513	-3.057015
H	0.335924	-6.212132	0.064259
H	-2.813698	-4.912628	-1.414693
H	-0.939293	-6.527020	-1.141237
H	-1.253344	-5.425117	0.227123
H	0.255543	-0.454589	3.415715
H	-2.417381	-1.141518	0.083689
H	-1.349387	1.108650	4.381246
H	-4.042074	0.404107	1.089978
H	-3.541599	1.559039	3.254241

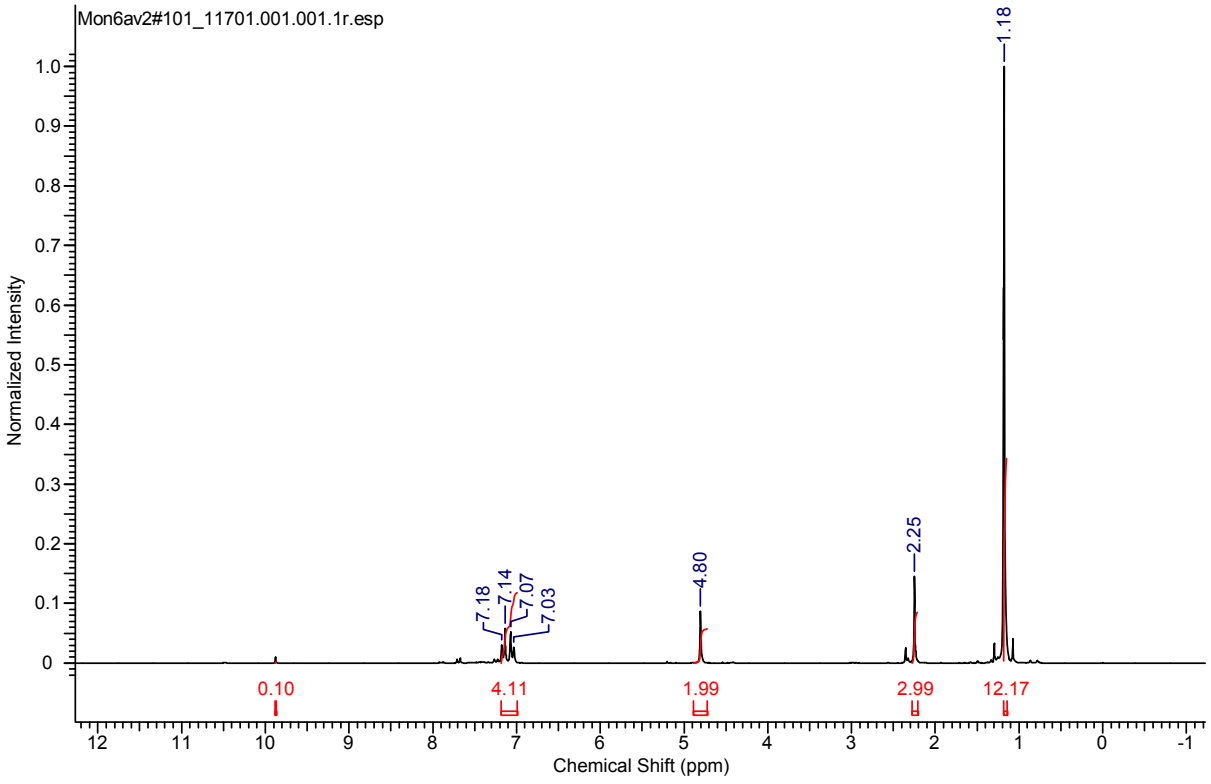
^{1}H NMR Spectrum of **2** ($CDCl_3$, 200 MHz, 298 K)



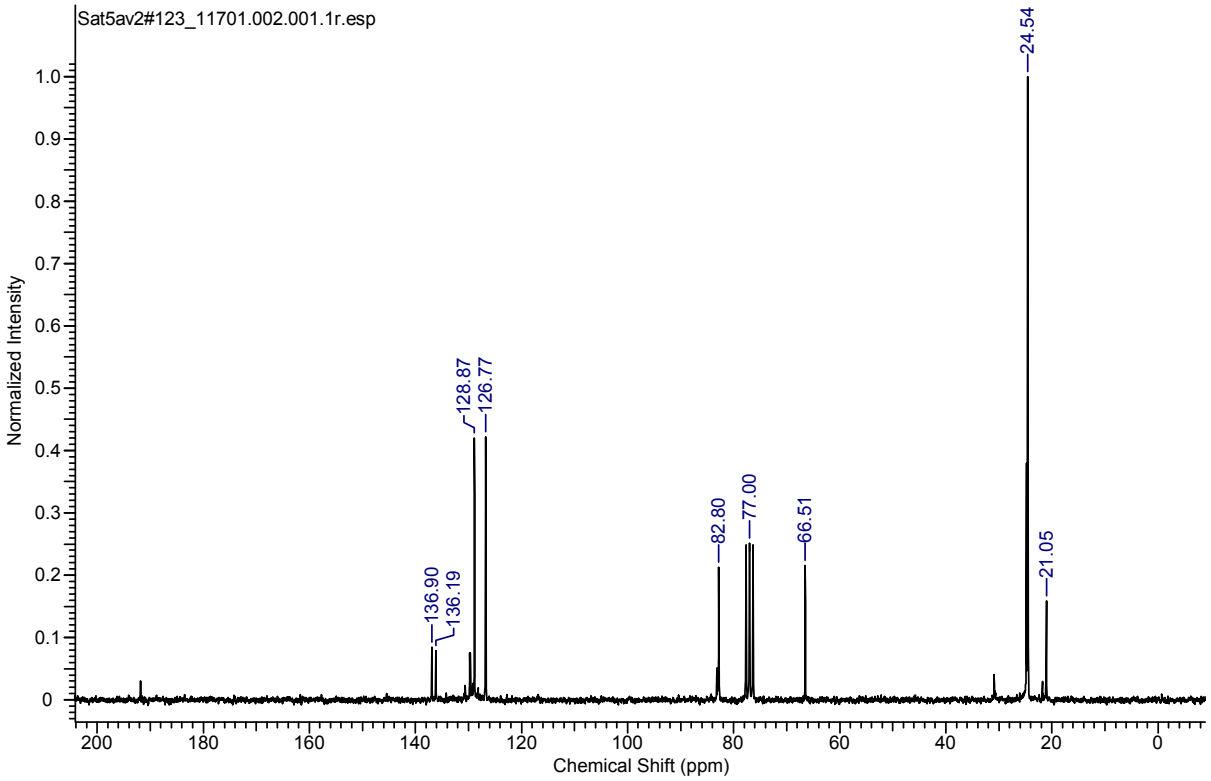
^{13}C NMR spectrum of **2** ($CDCl_3$, 50.28 MHz, 298 K)



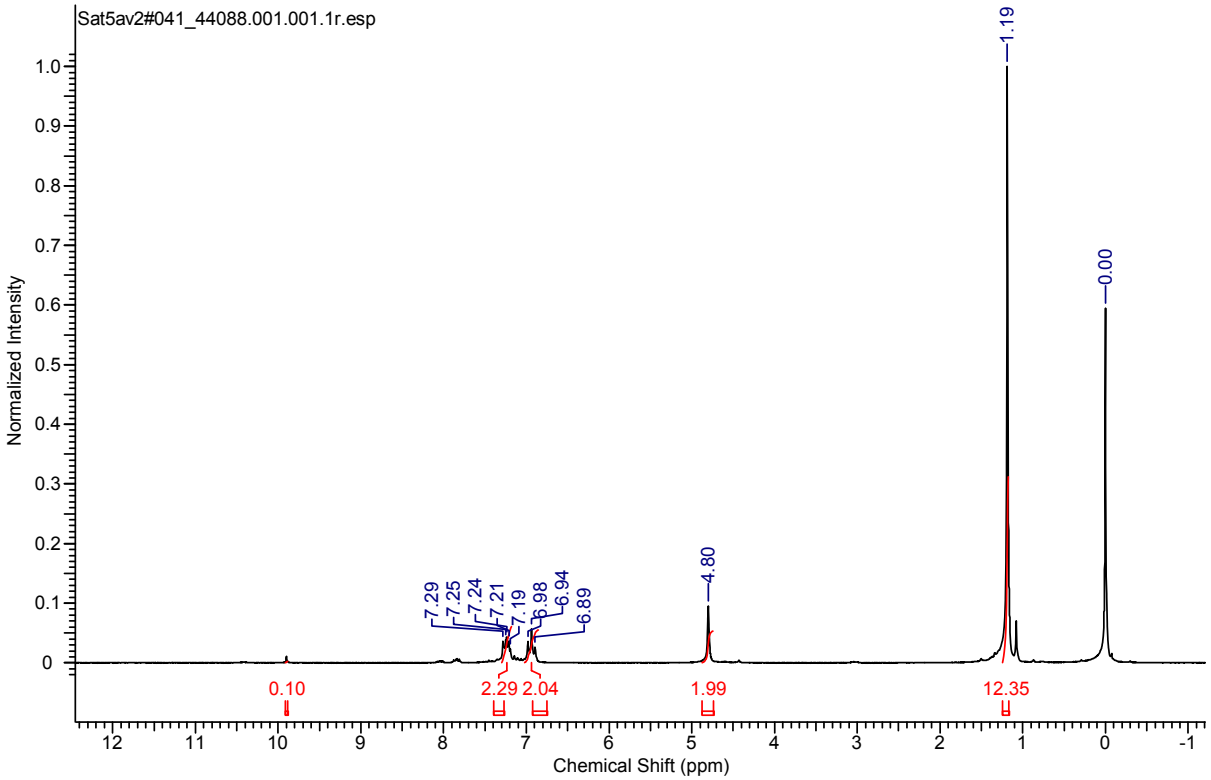
^{1}H NMR Spectrum of **3** ($CDCl_3$, 200 MHz, 298 K)



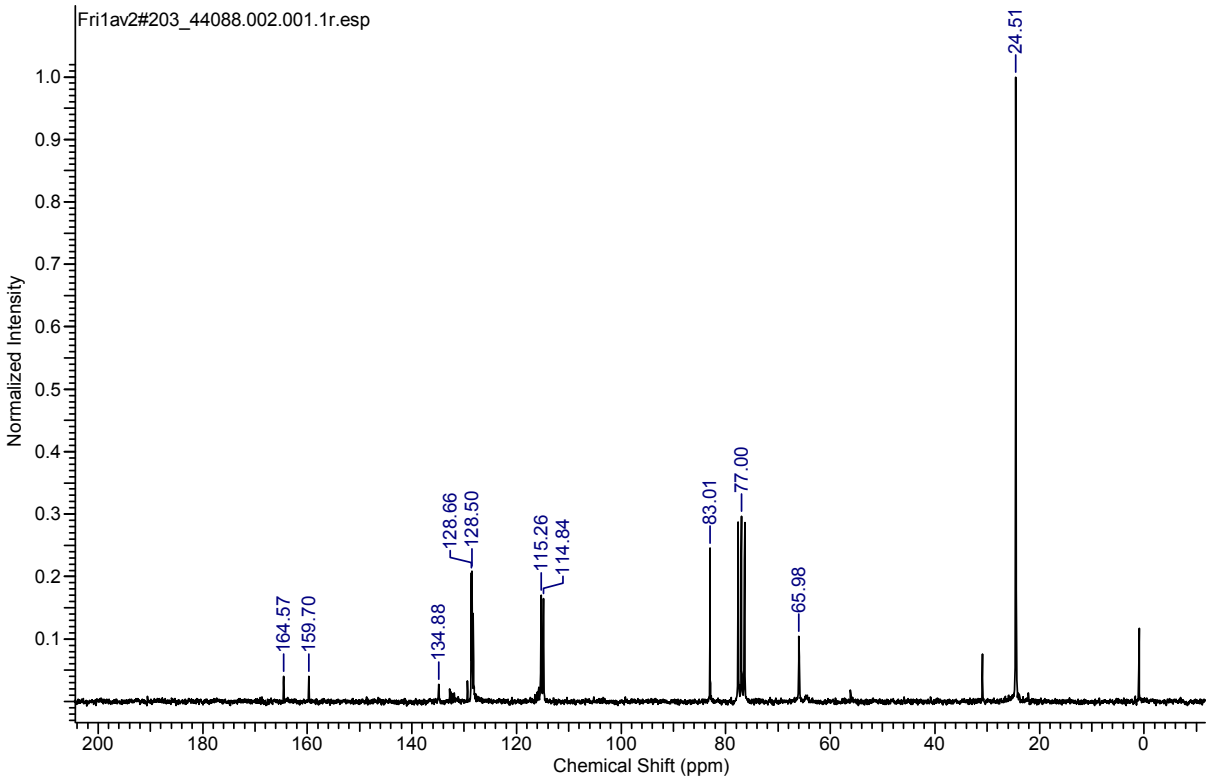
^{13}C NMR spectrum of **3** ($CDCl_3$, 50.28 MHz, 298 K)



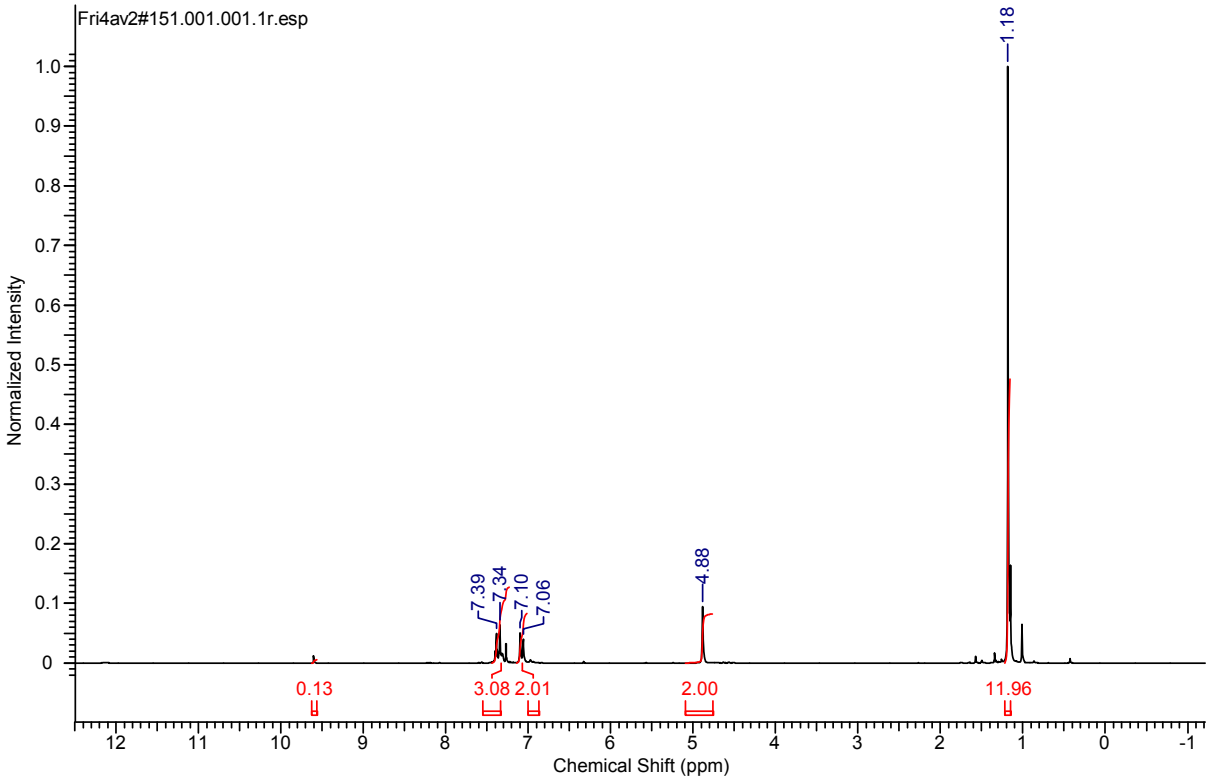
^{1}H NMR Spectrum of **4** ($CDCl_3$, 200 MHz, 298 K)



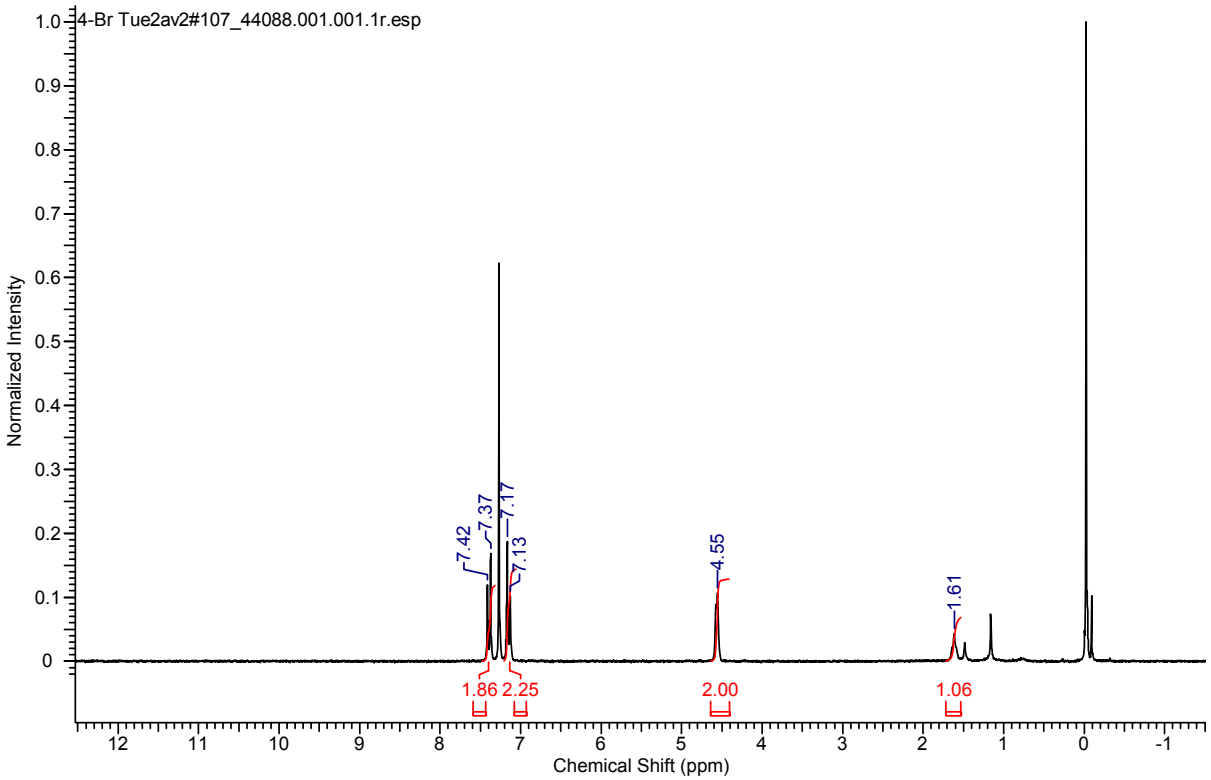
^{13}C NMR spectrum of **4** ($CDCl_3$, 50.28 MHz, 298 K)



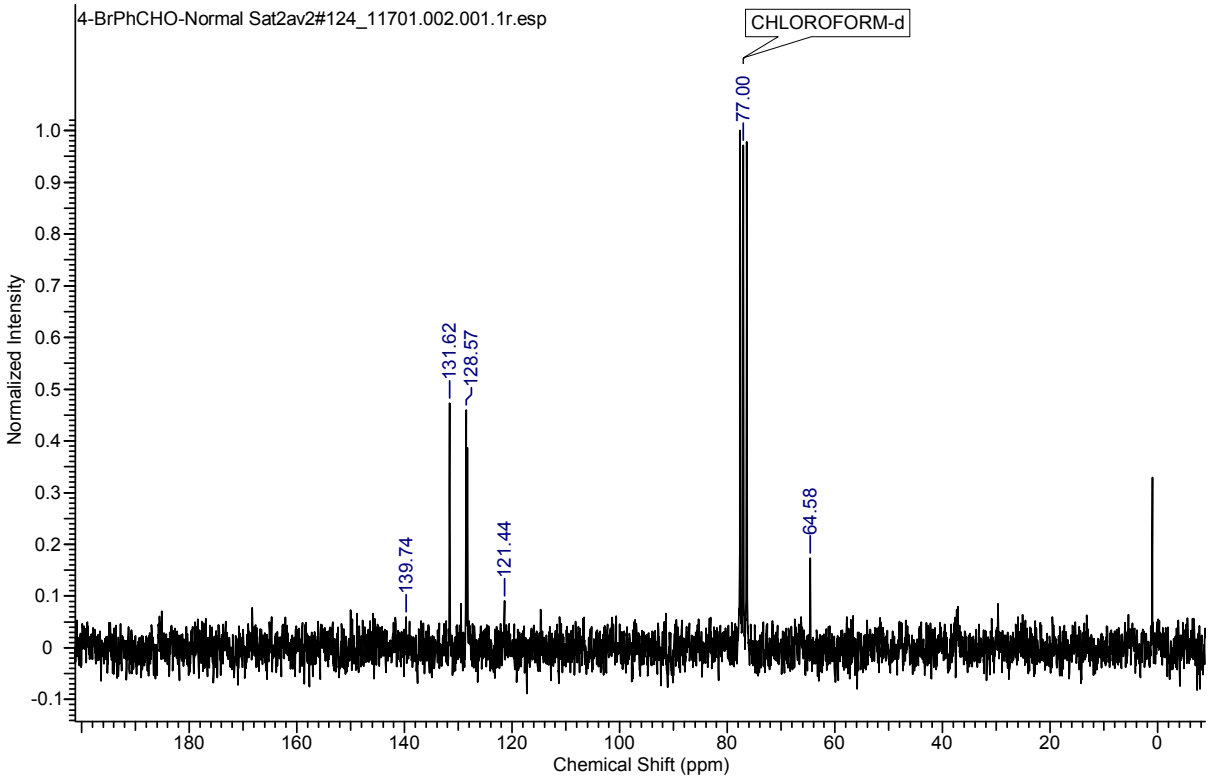
^{1}H NMR Spectrum of **5** ($CDCl_3$, 200 MHz, 298 K)



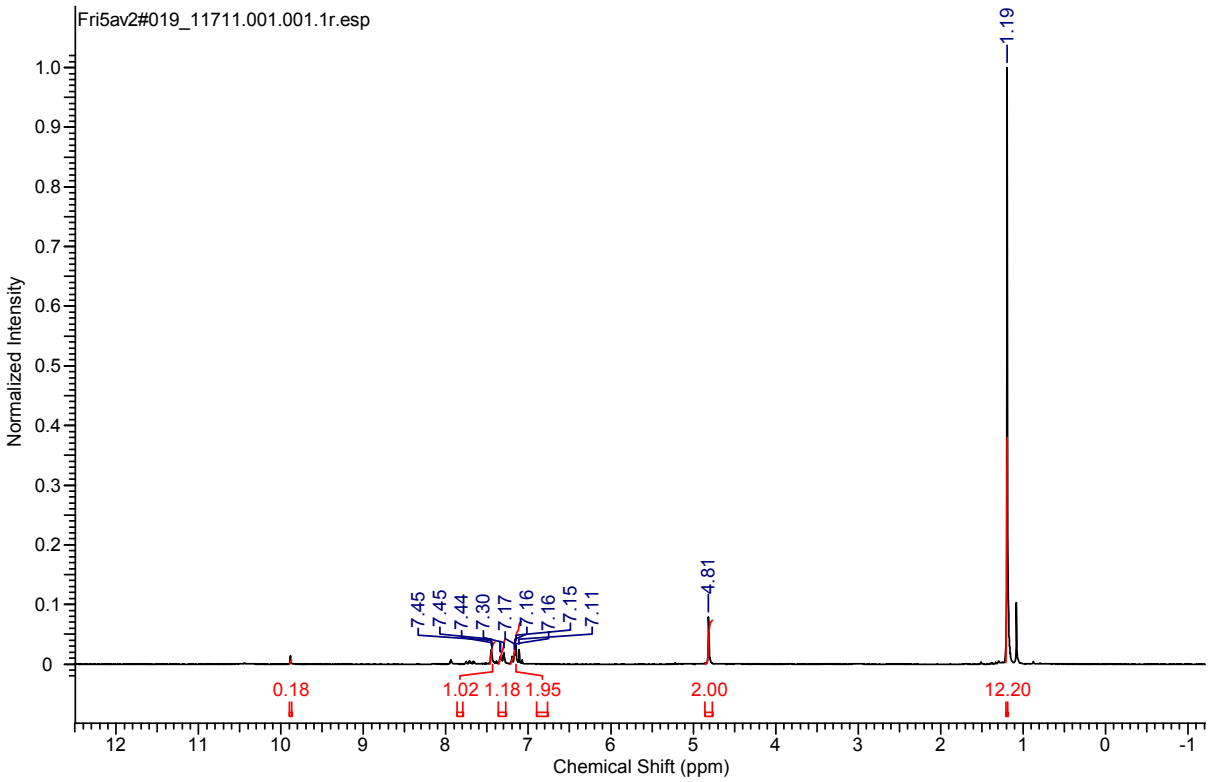
^{1}H NMR Spectrum of **5' (Isolated)** ($CDCl_3$, 200 MHz, 298 K)



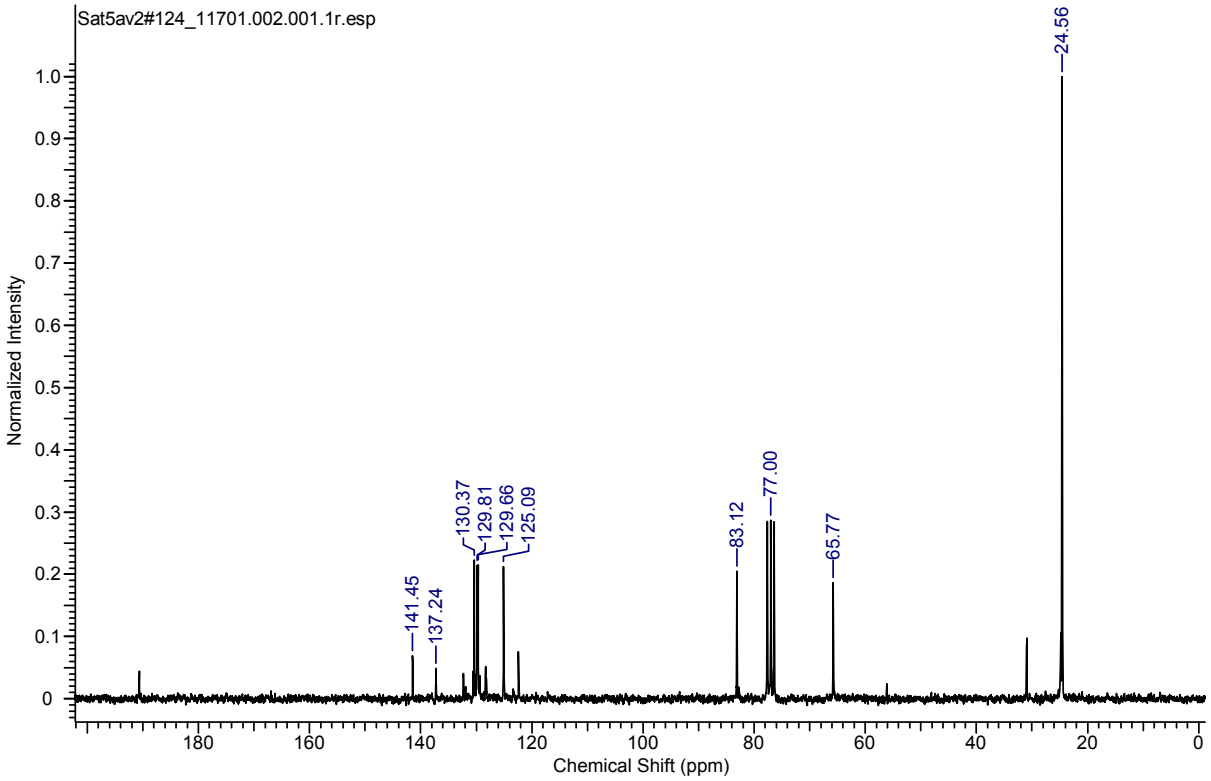
^{13}C NMR spectrum of **5' (Isolated)** ($CDCl_3$, 50.28 MHz, 298 K)



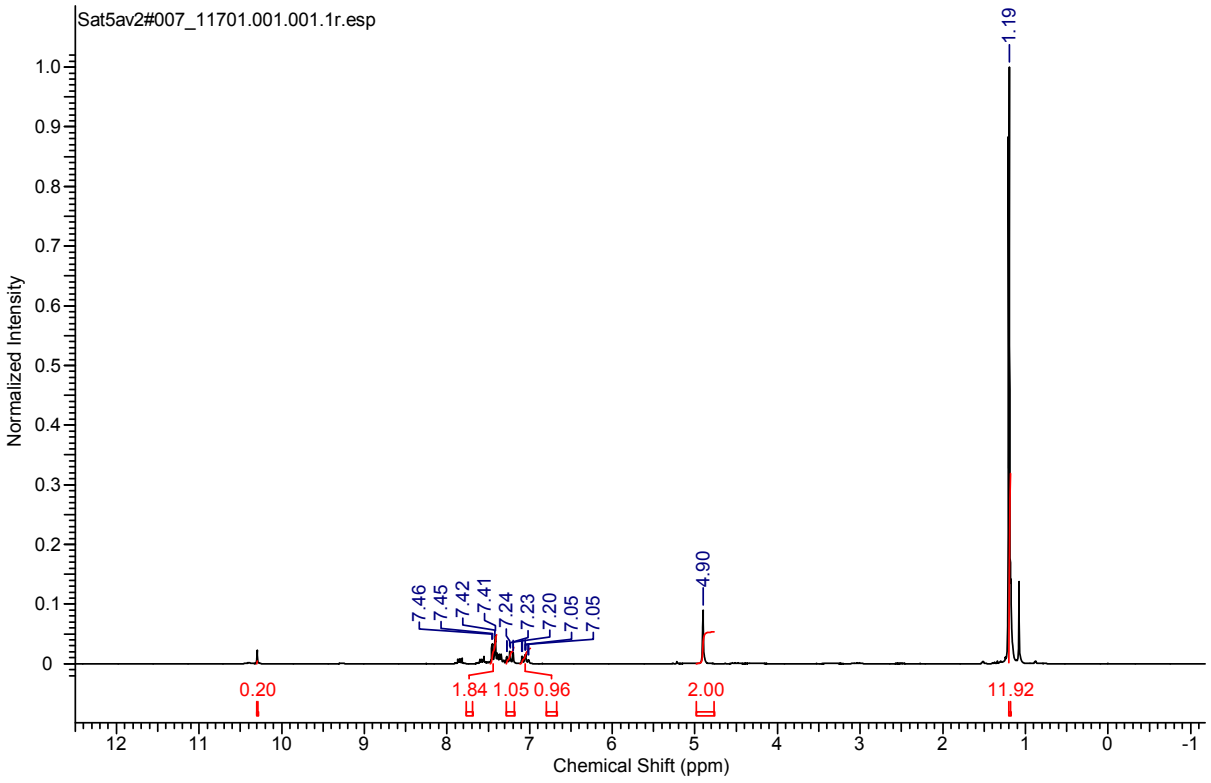
^{1}H NMR Spectrum of **6** ($CDCl_3$, 200 MHz, 298 K)



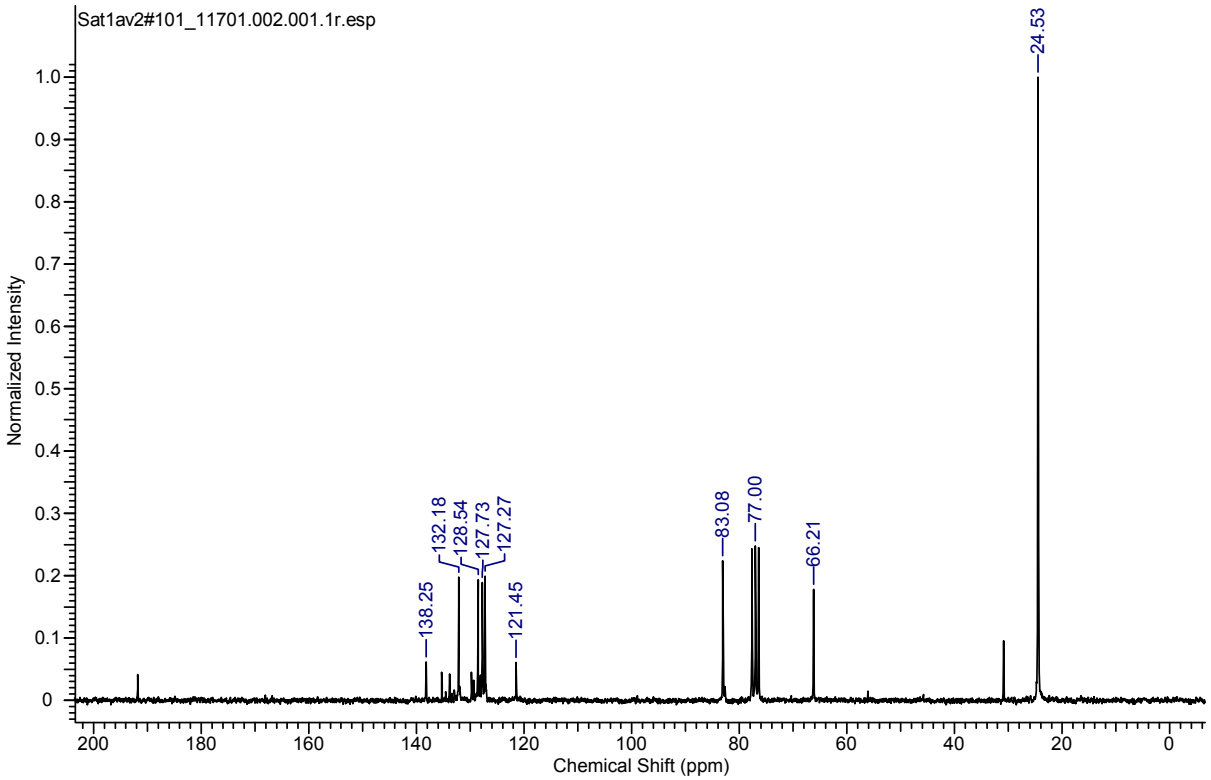
^{13}C NMR spectrum of **6** ($CDCl_3$, 50.28 MHz, 298 K)



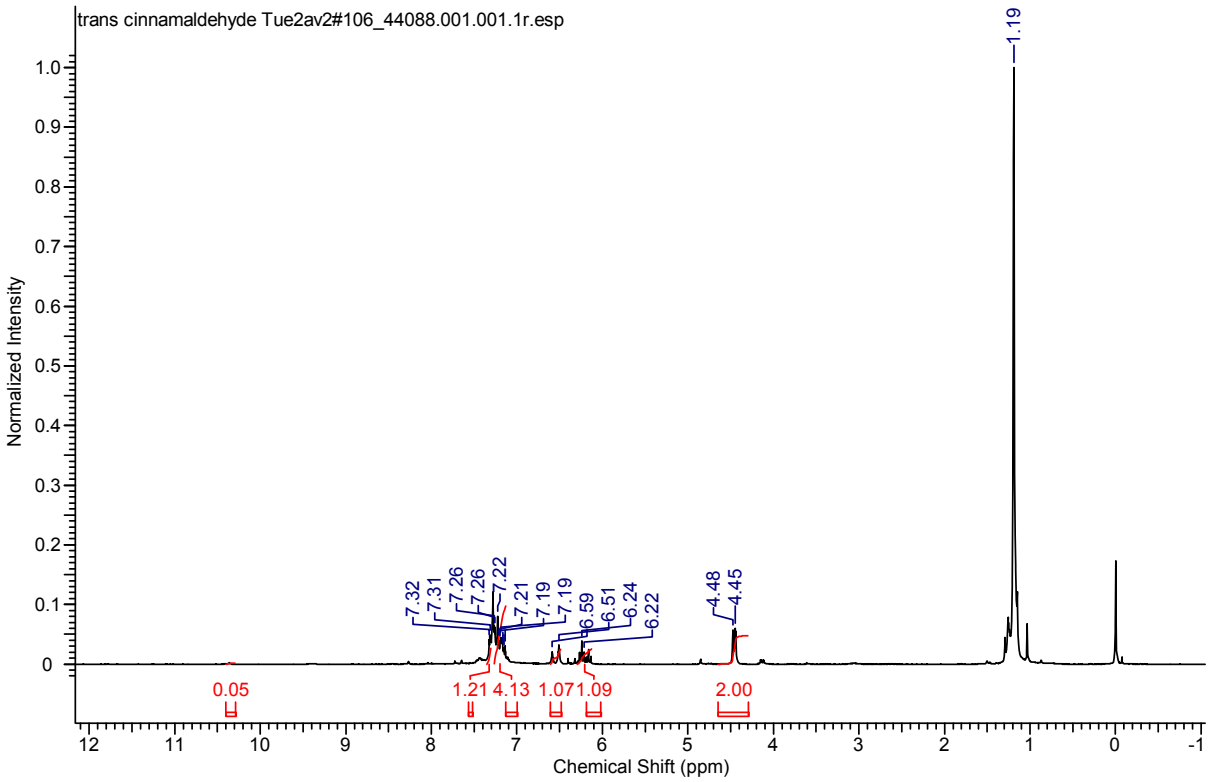
^{1}H NMR Spectrum of **7** ($CDCl_3$, 200 MHz, 298 K)



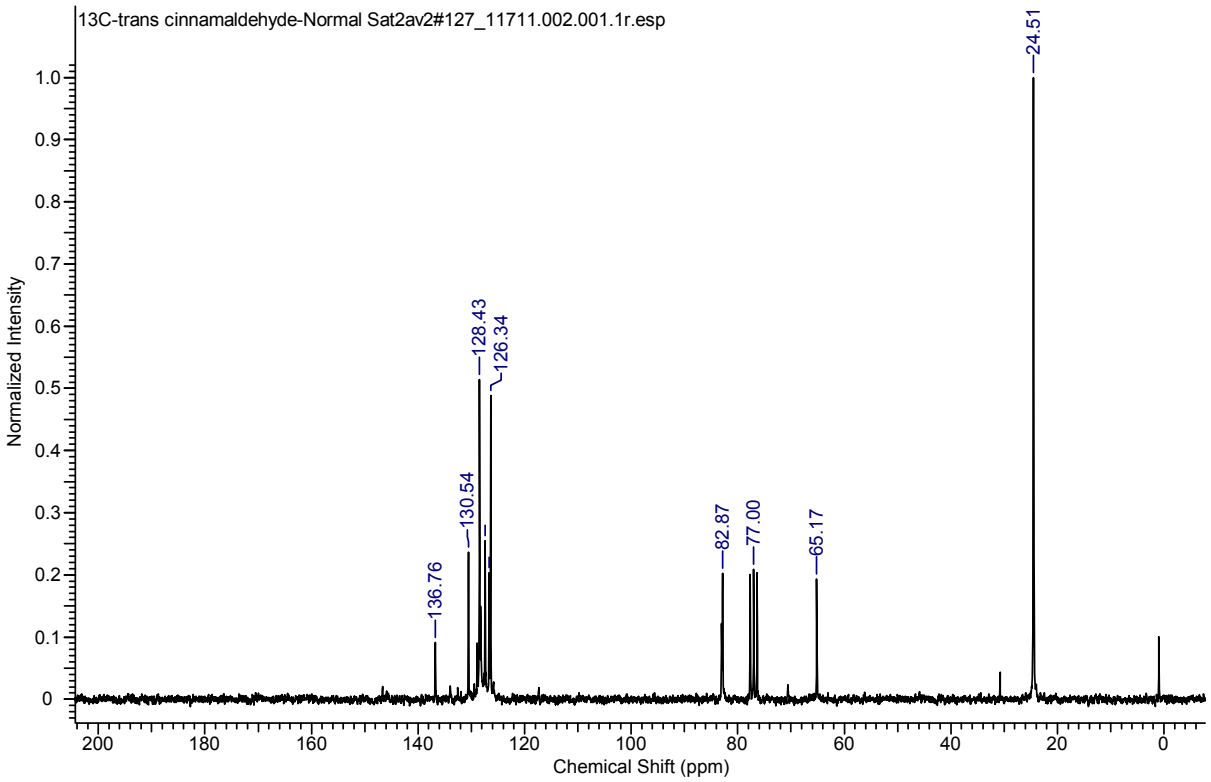
^{13}C NMR spectrum of **7** ($CDCl_3$, 50.28 MHz, 298 K)



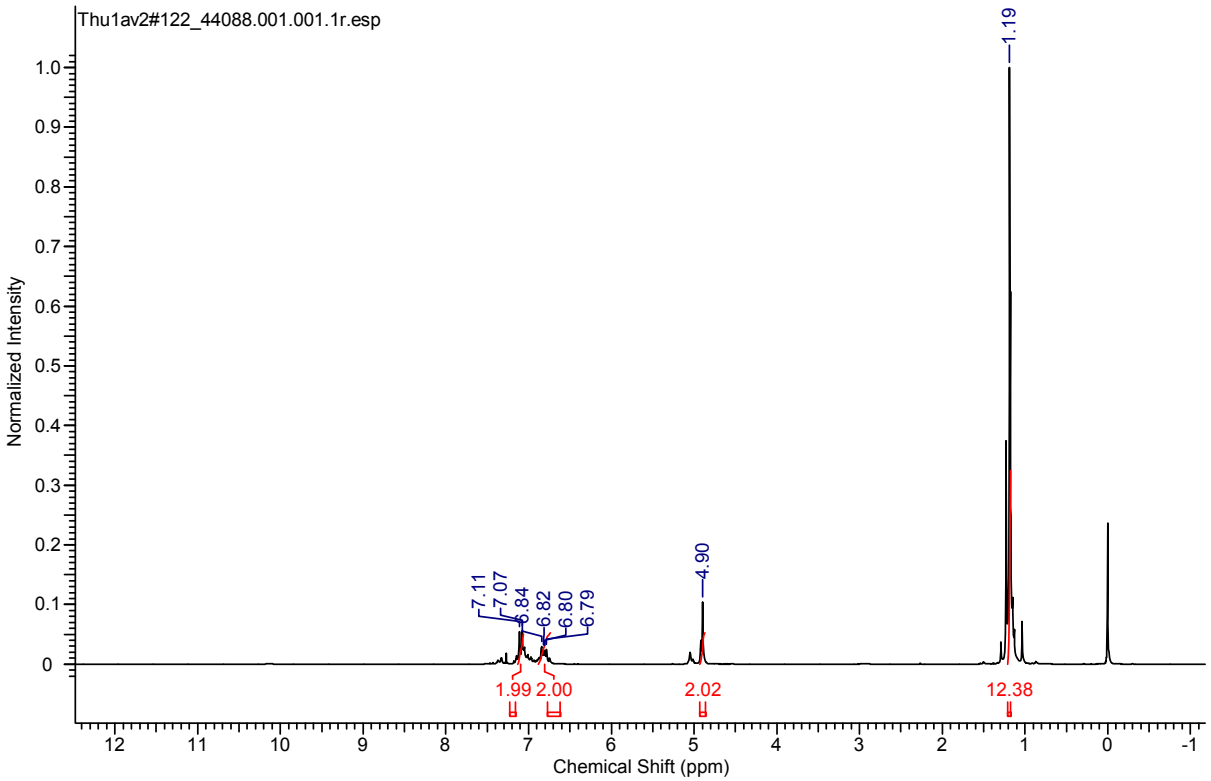
^{1}H NMR Spectrum of **8** ($CDCl_3$, 200 MHz, 298 K)



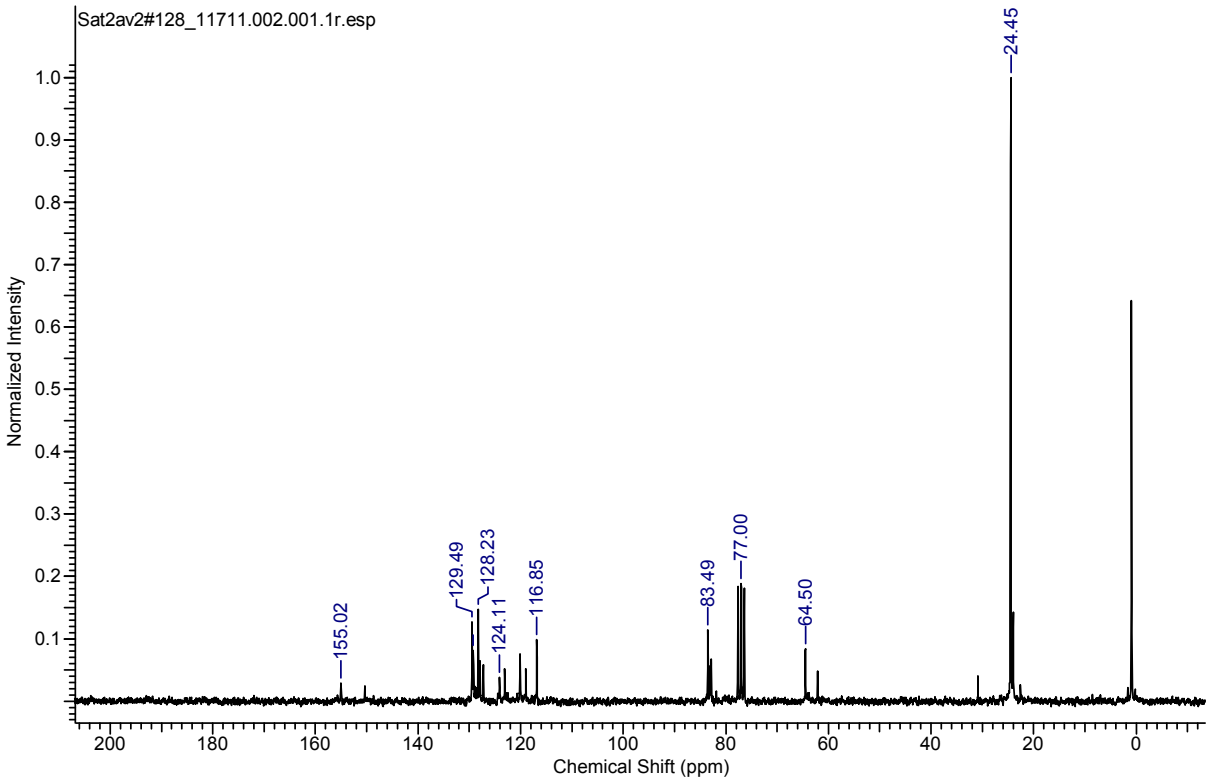
^{13}C NMR spectrum of **8** ($CDCl_3$, 50.28 MHz, 298 K)



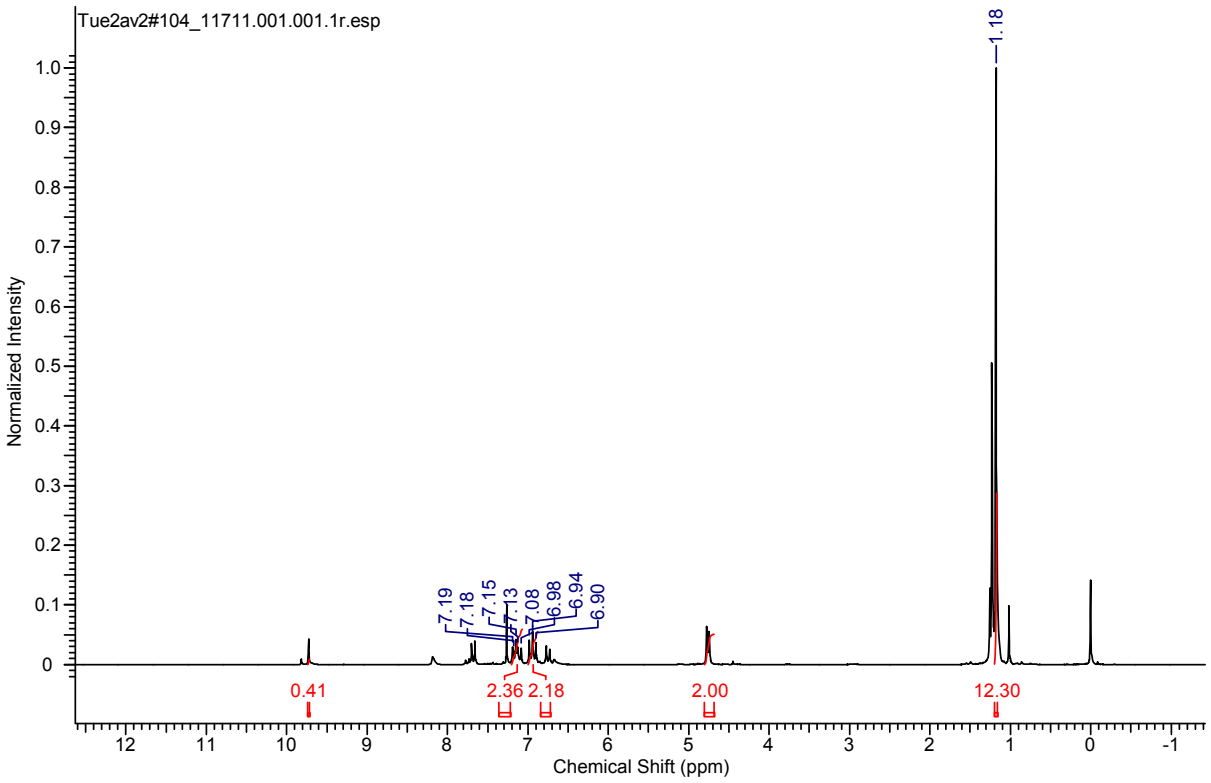
^{1}H NMR Spectrum of **9** ($CDCl_3$, 200 MHz, 298 K)



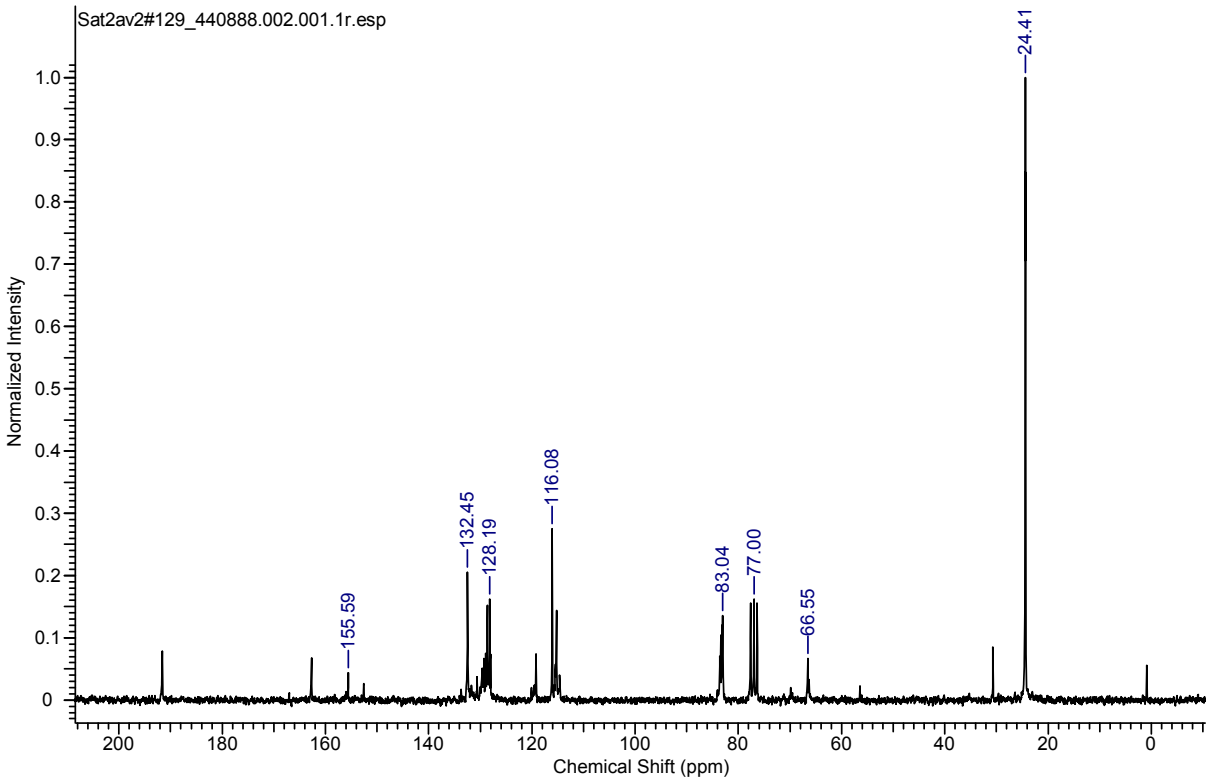
^{13}C NMR spectrum of **9** ($CDCl_3$, 50.28 MHz, 298 K)



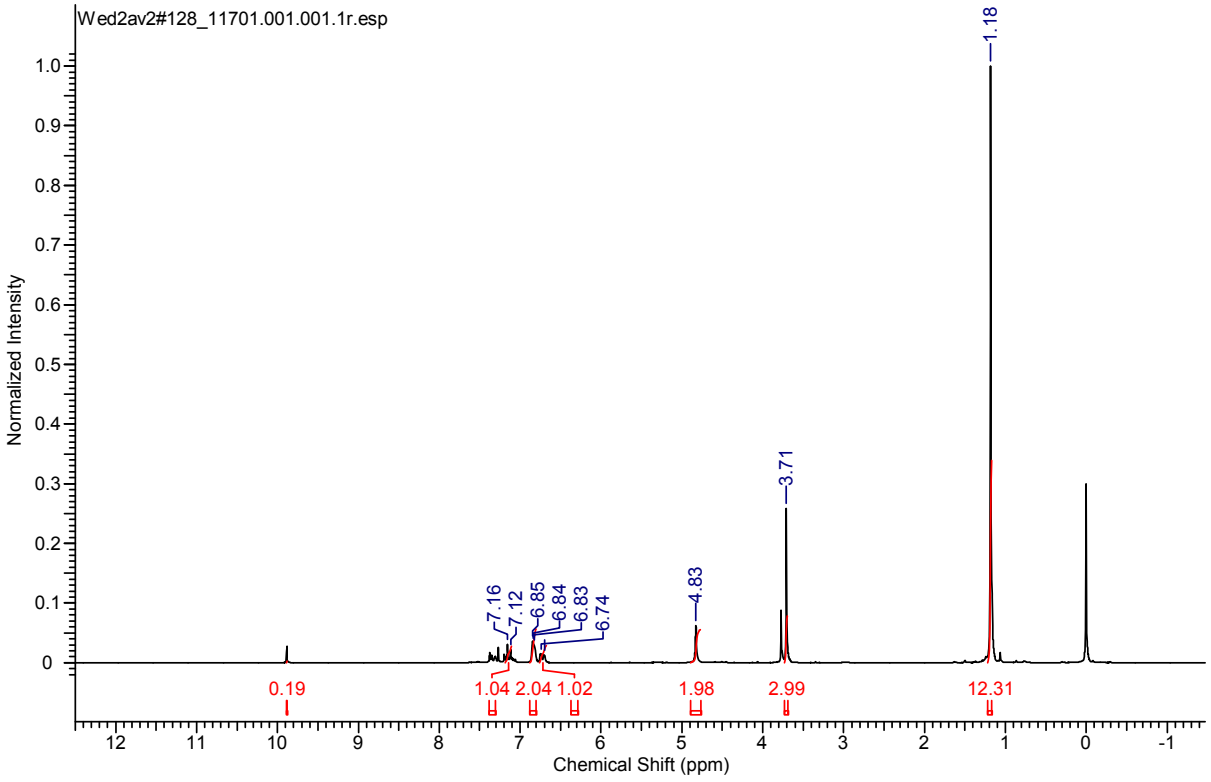
^{1}H NMR Spectrum of **10** ($CDCl_3$, 200 MHz, 298 K)



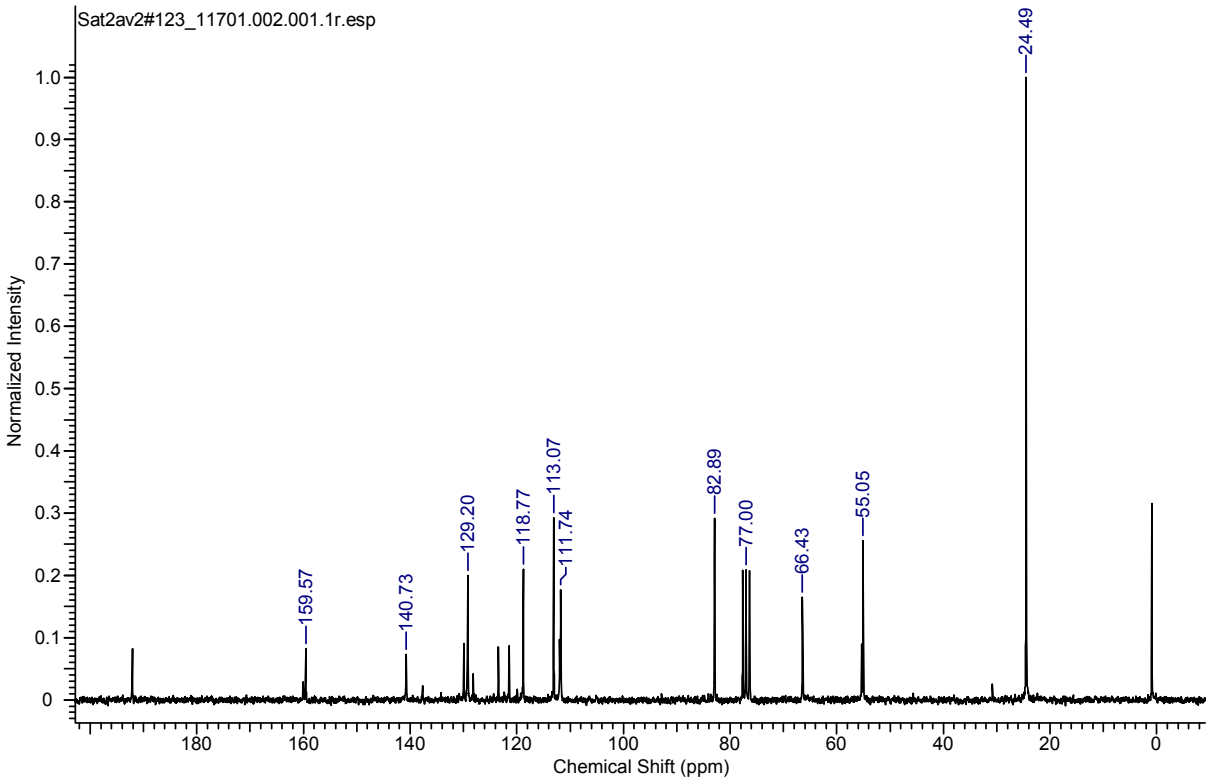
^{13}C NMR spectrum of **10** ($CDCl_3$, 50.28 MHz, 298 K)



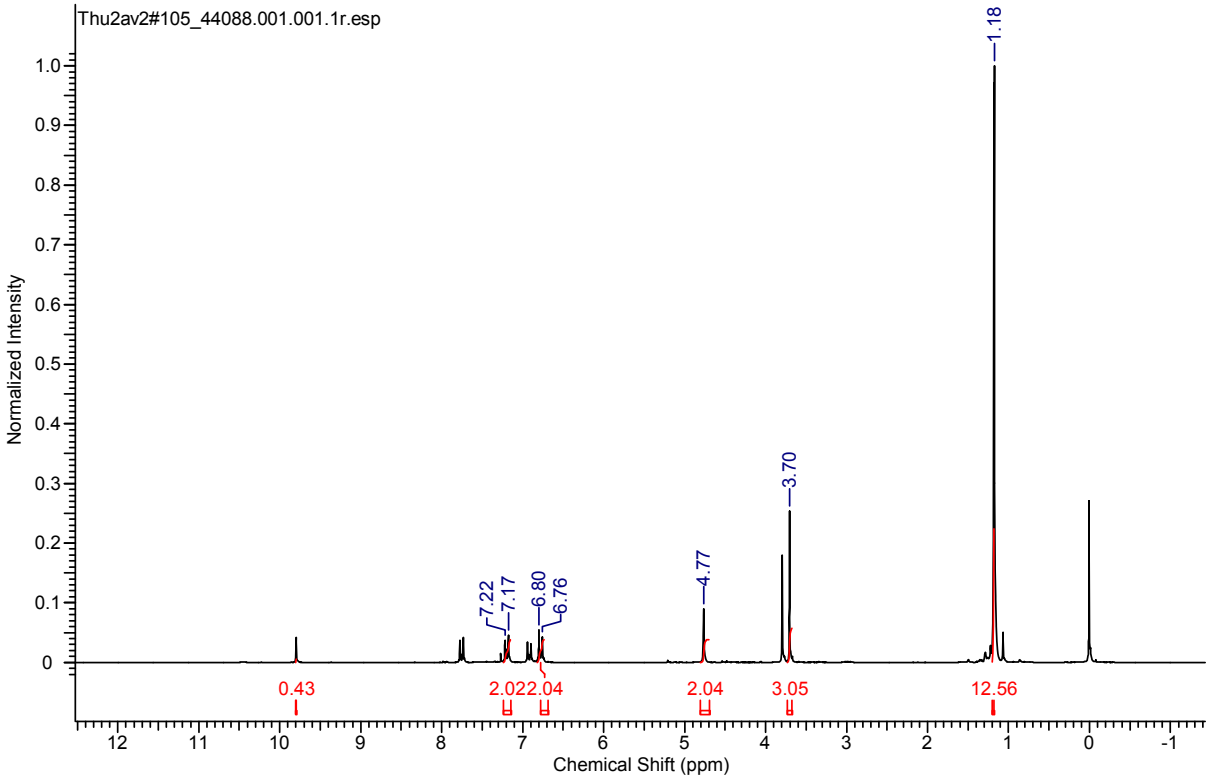
^{1}H NMR Spectrum of **11** ($CDCl_3$, 200 MHz, 298 K)



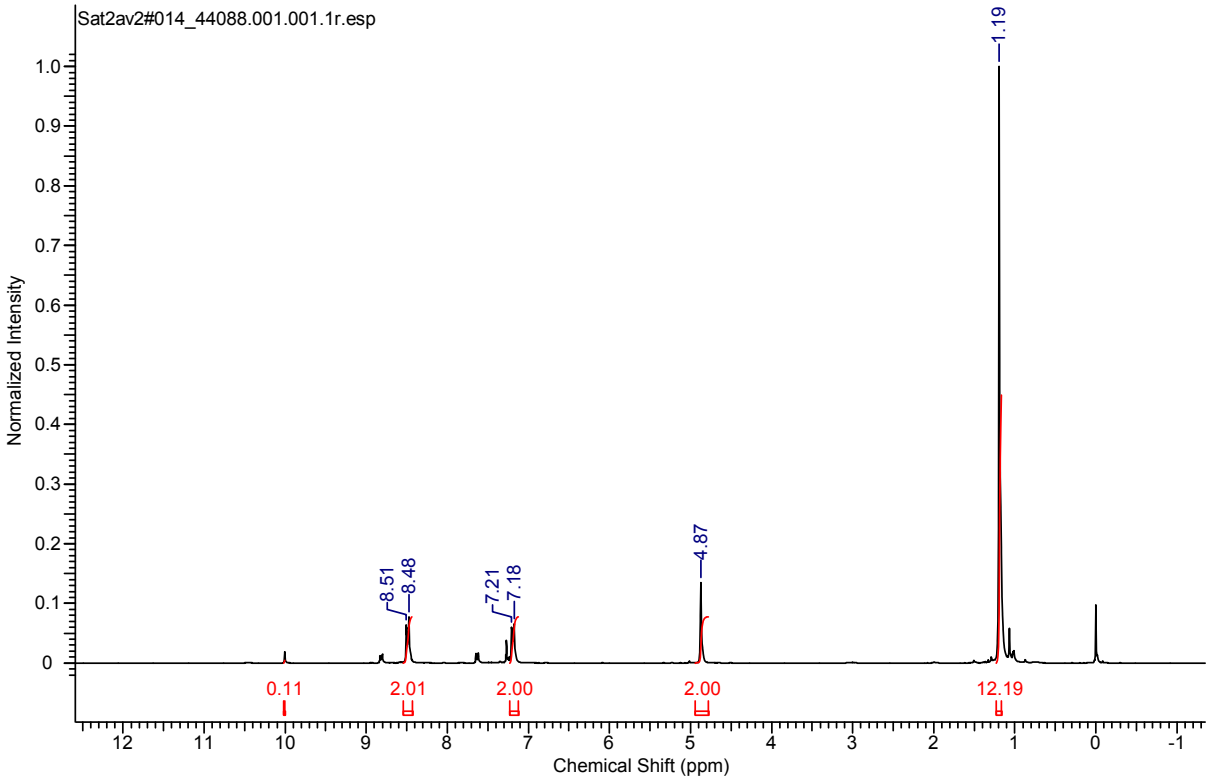
^{13}C NMR spectrum of **11** ($CDCl_3$, 50.28 MHz, 298 K)



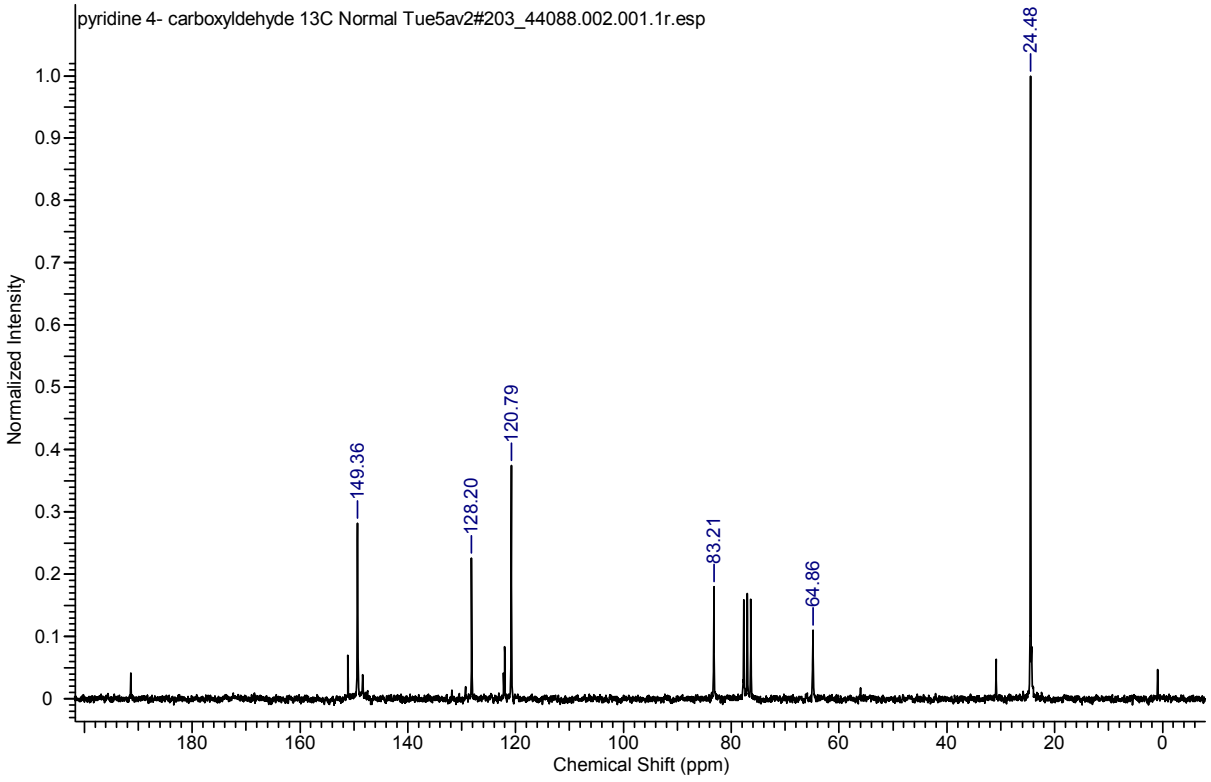
^{1}H NMR Spectrum of **12** ($CDCl_3$, 200 MHz, 298 K)



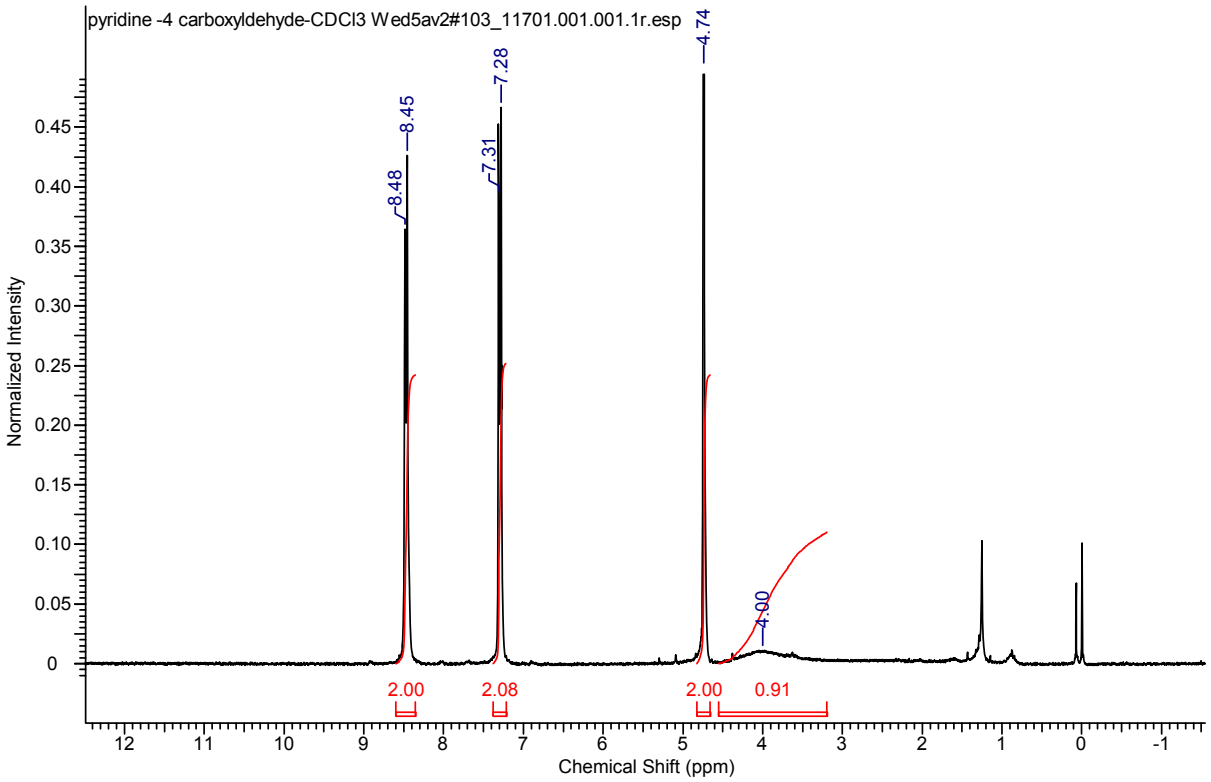
^{1}H NMR Spectrum of **13** ($CDCl_3$, 200 MHz, 298 K)



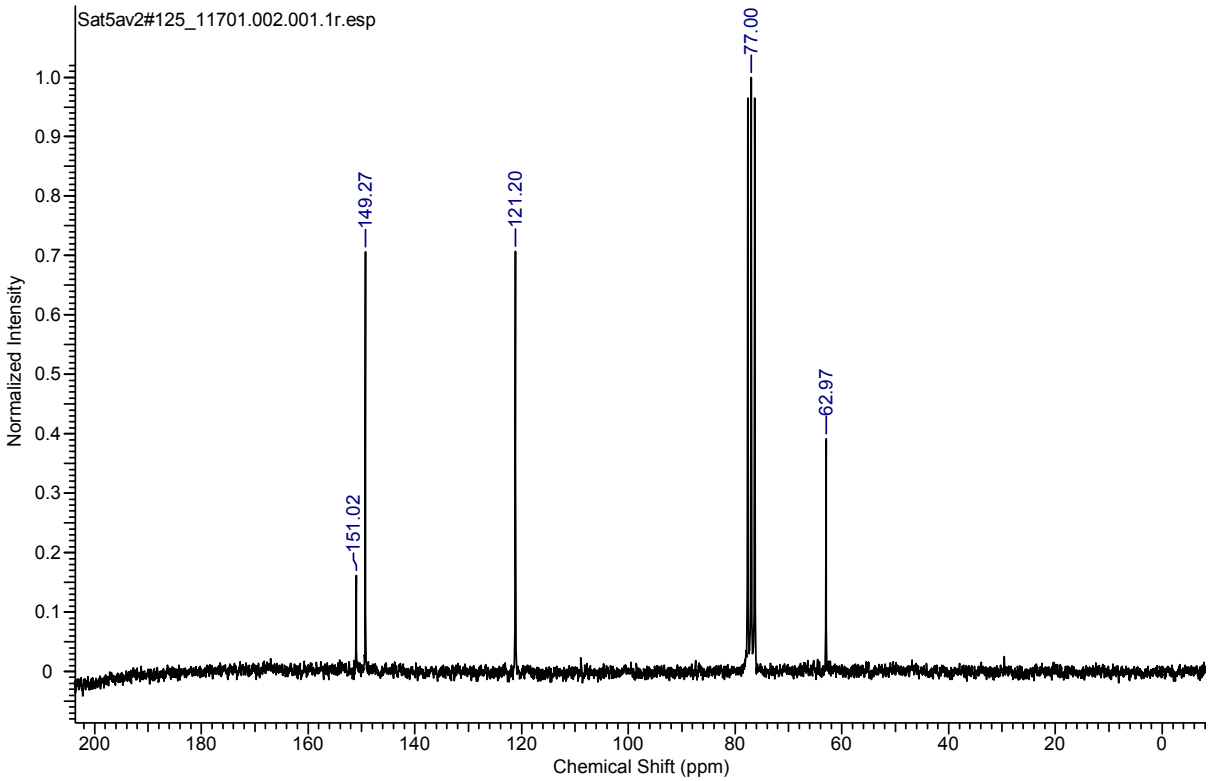
^{13}C NMR spectrum of **13** ($CDCl_3$, 50.28 MHz, 298 K)



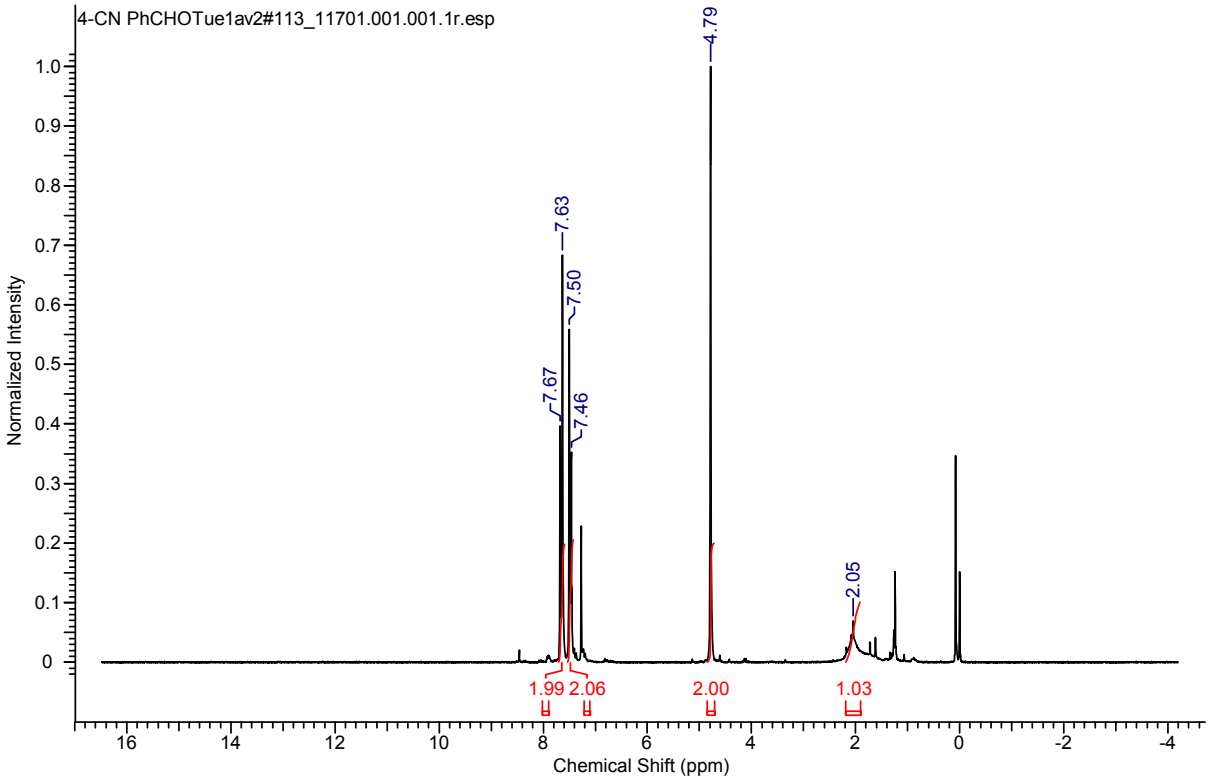
^{1}H NMR Spectrum of **13' (Isolated)** ($CDCl_3$, 200 MHz, 298 K)



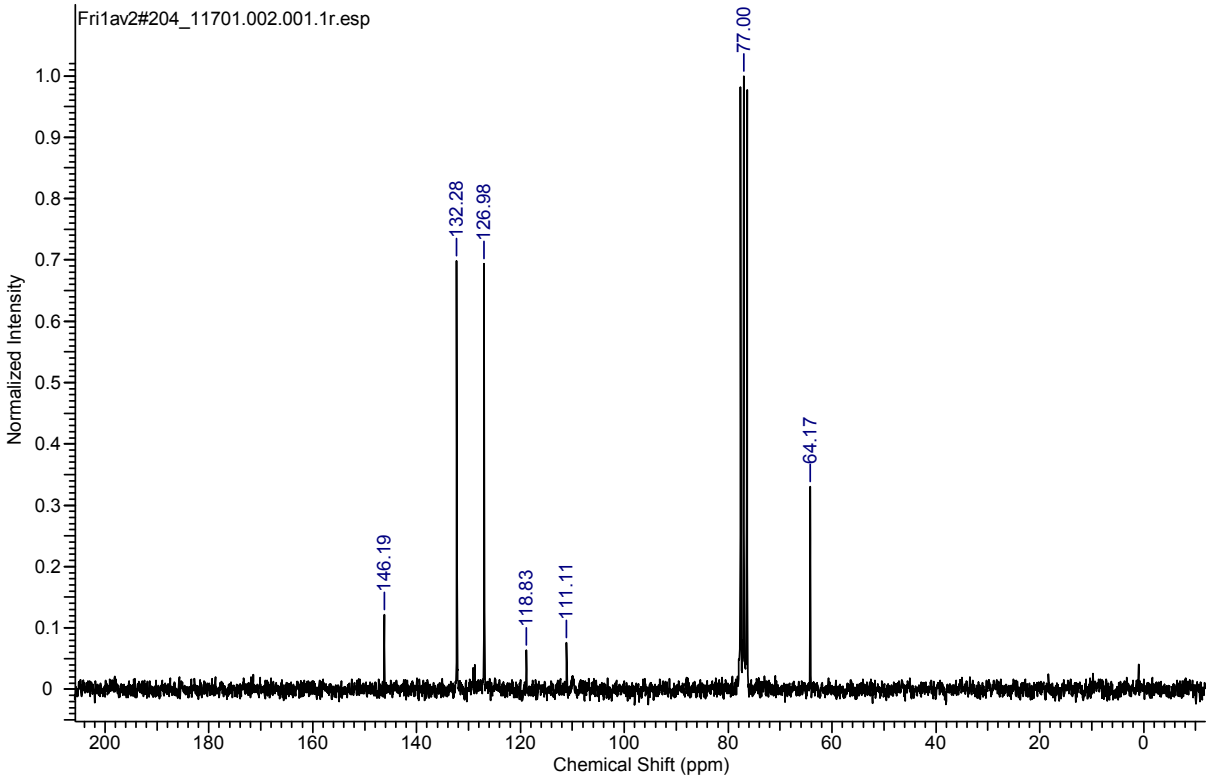
^{13}C NMR spectrum of **13' (Isolated)** ($CDCl_3$, 50.28 MHz, 298 K)



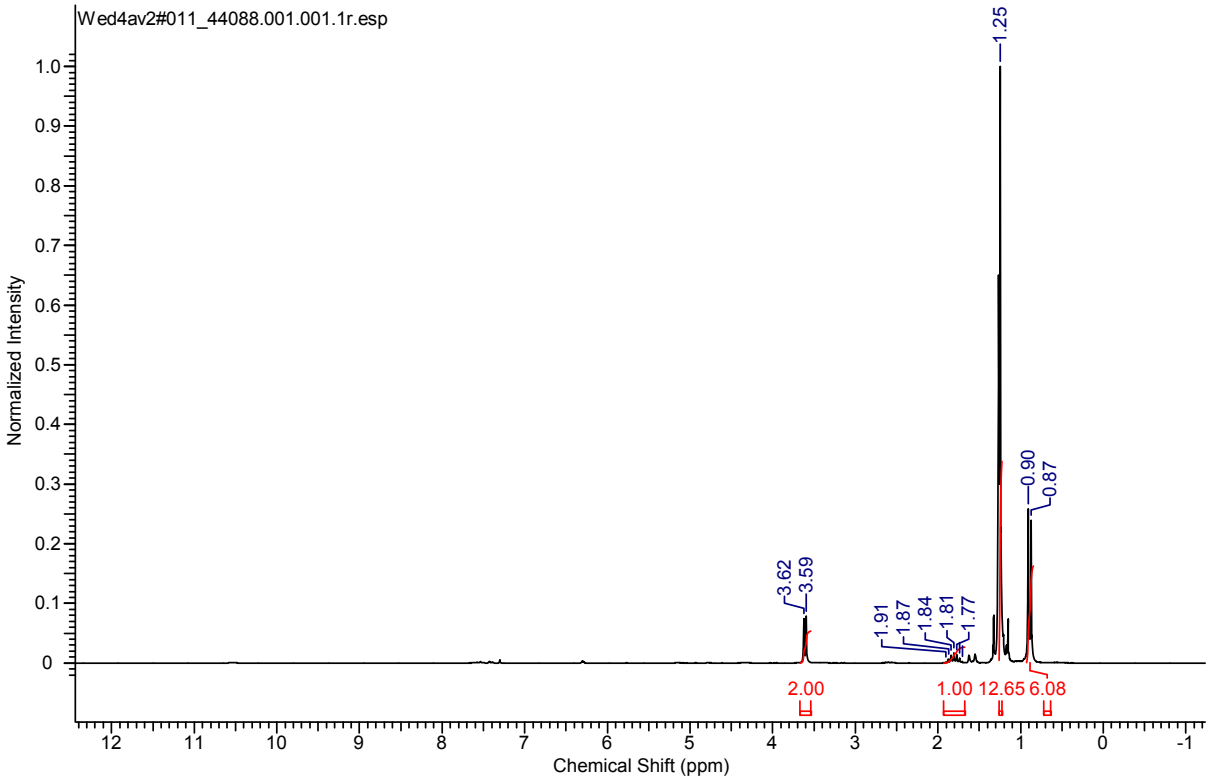
^{1}H NMR Spectrum of **14' (Isolated)** ($CDCl_3$, 200 MHz, 298 K)



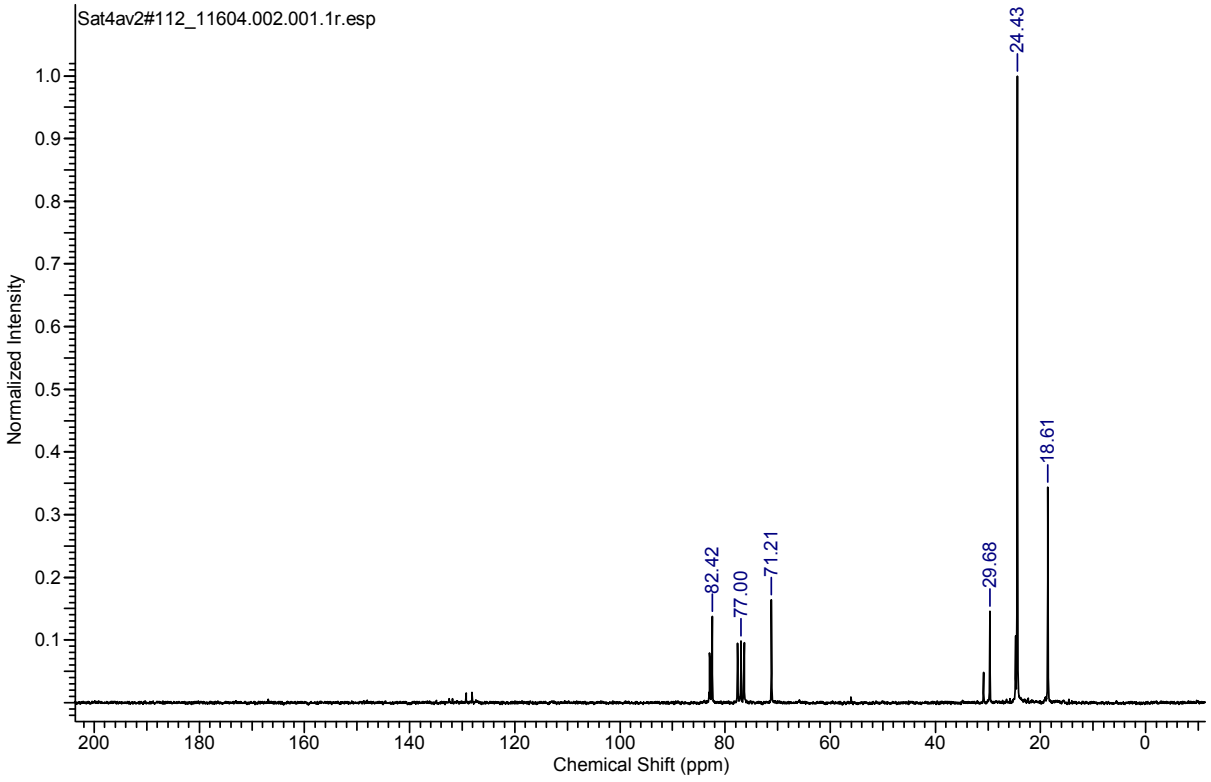
^{13}C NMR spectrum of **14' (Isolated)** ($CDCl_3$, 50.28 MHz, 298 K)



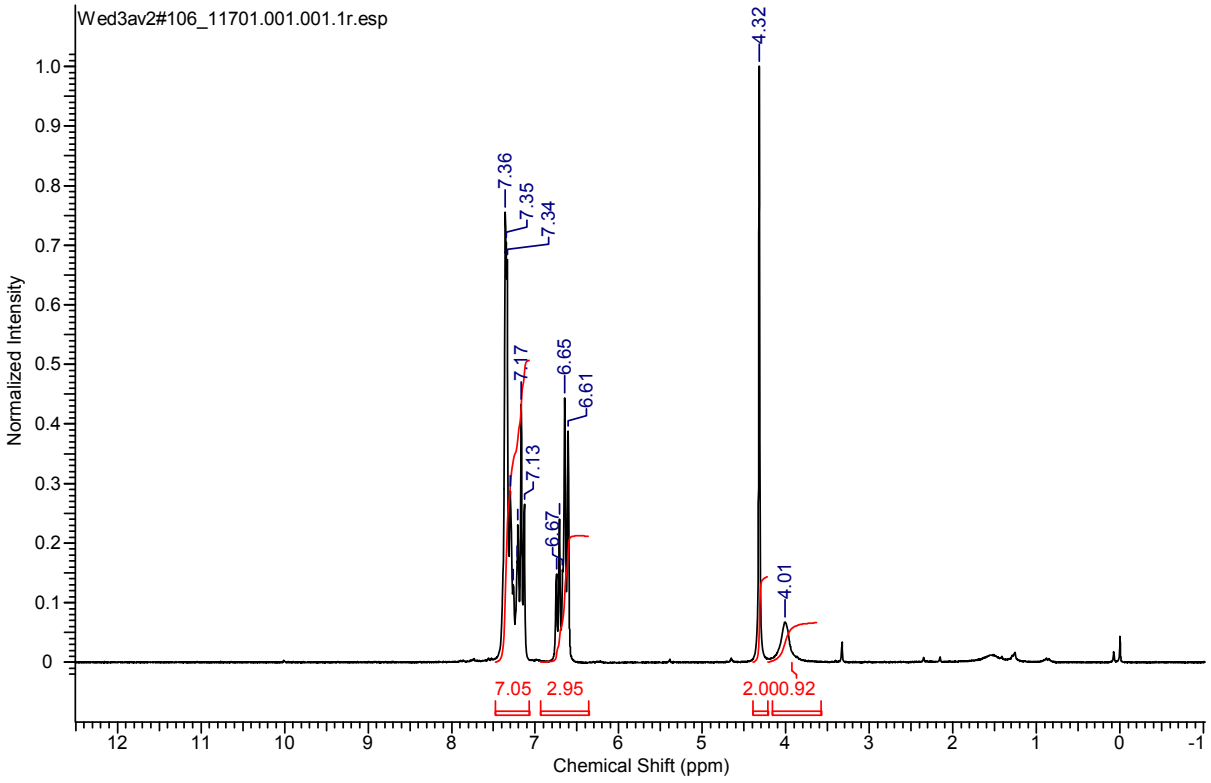
^{1}H NMR Spectrum of **15** ($CDCl_3$, 200 MHz, 298 K)



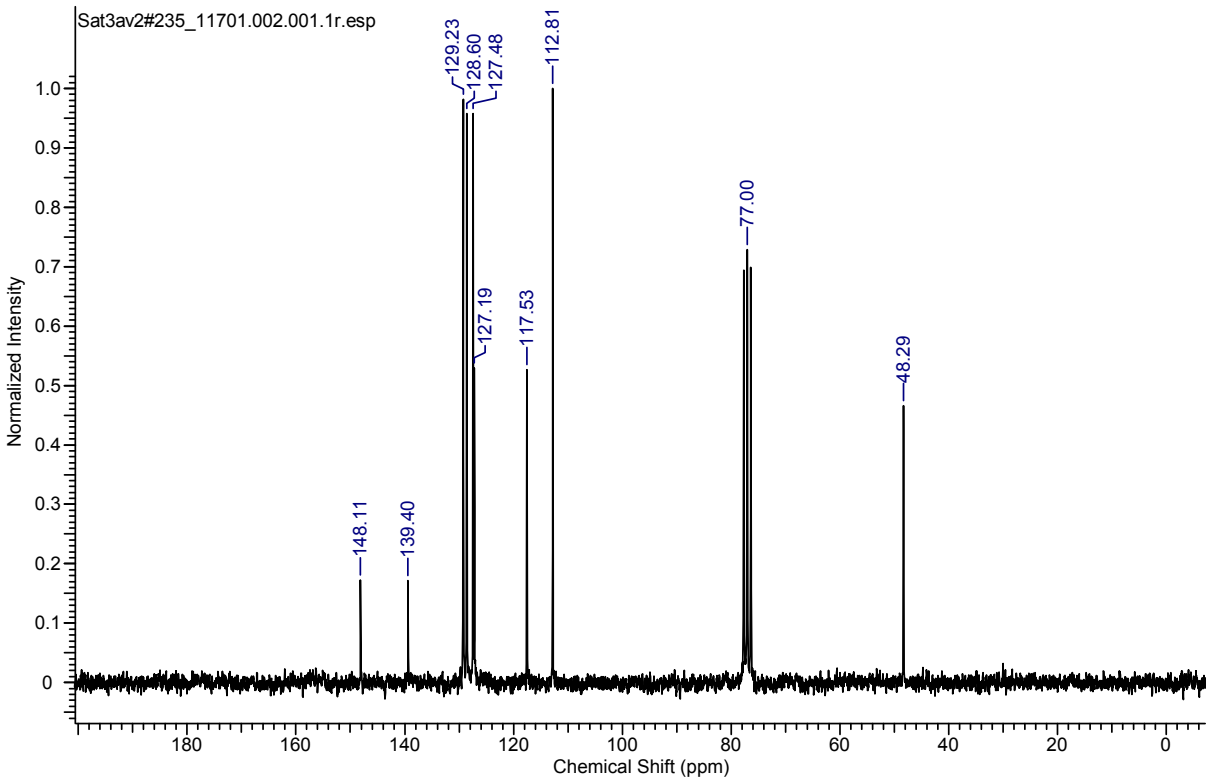
^{13}C NMR spectrum of **15** ($CDCl_3$, 50.28 MHz, 298 K)



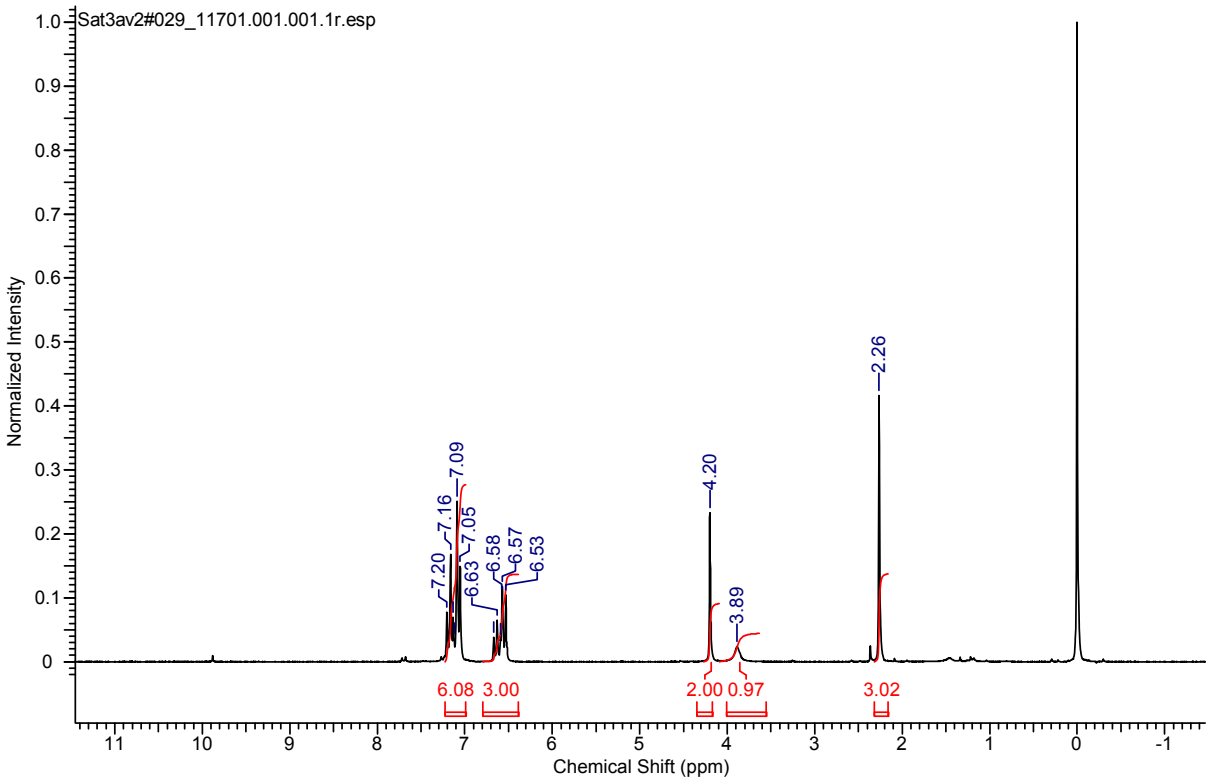
^{1}H NMR Spectrum of Isolated **N-benzylaniline (16)** ($CDCl_3$, 200 MHz, 298 K)



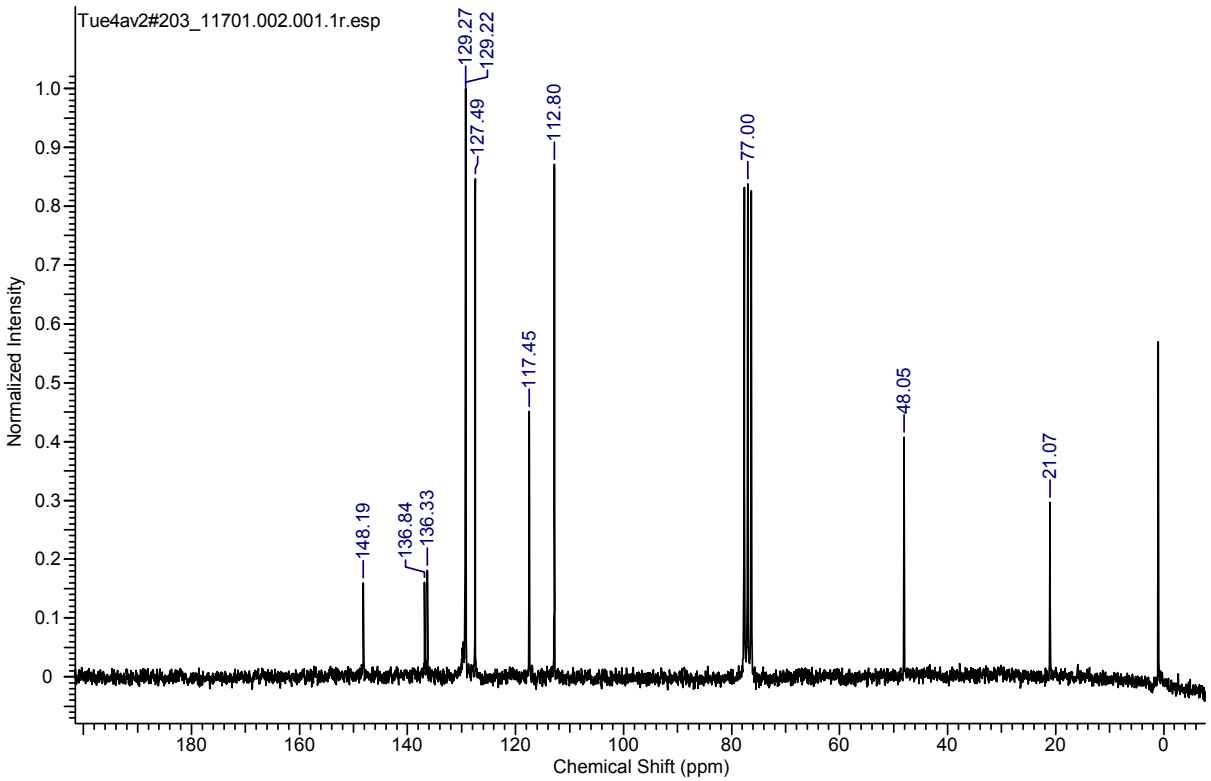
^{13}C NMR spectrum of Isolated **N-benzylaniline (16)** ($CDCl_3$, 50.28 MHz, 298 K)



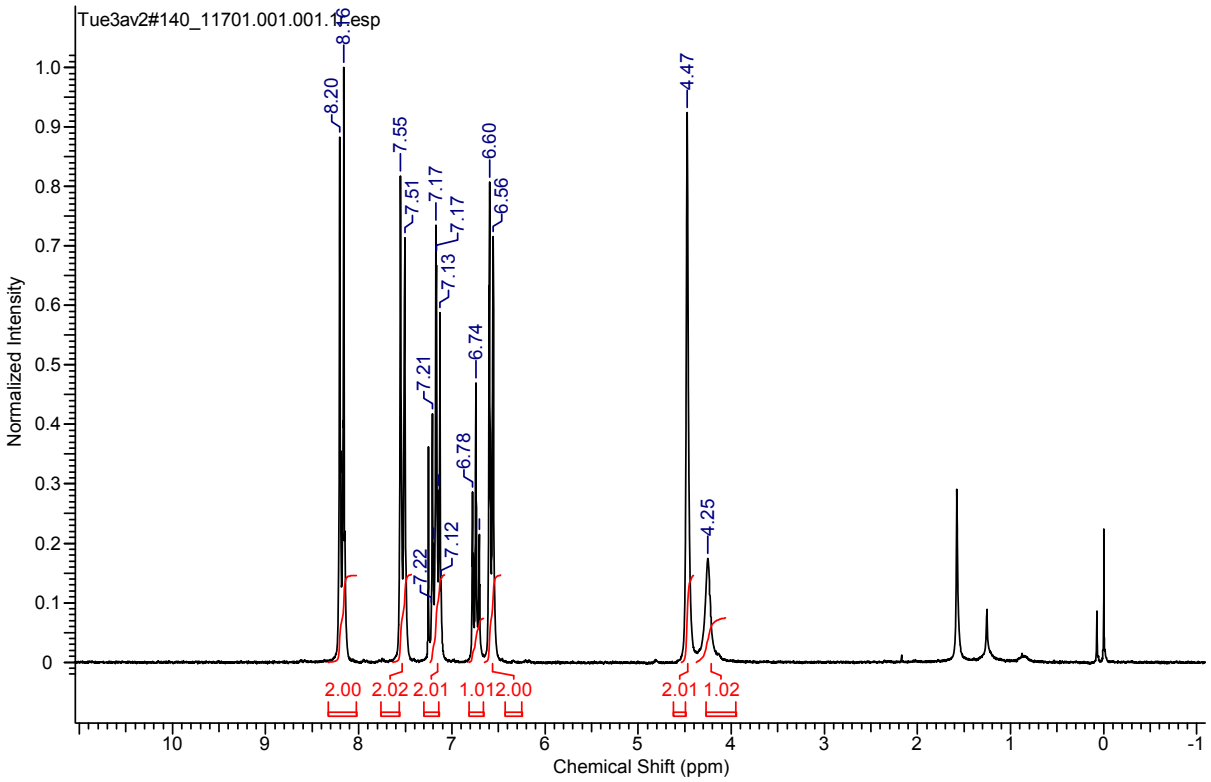
^{1}H NMR Spectrum of Isolated **N-(4-methylbenzyl)aniline (17)** ($CDCl_3$, 200 MHz, 298 K)



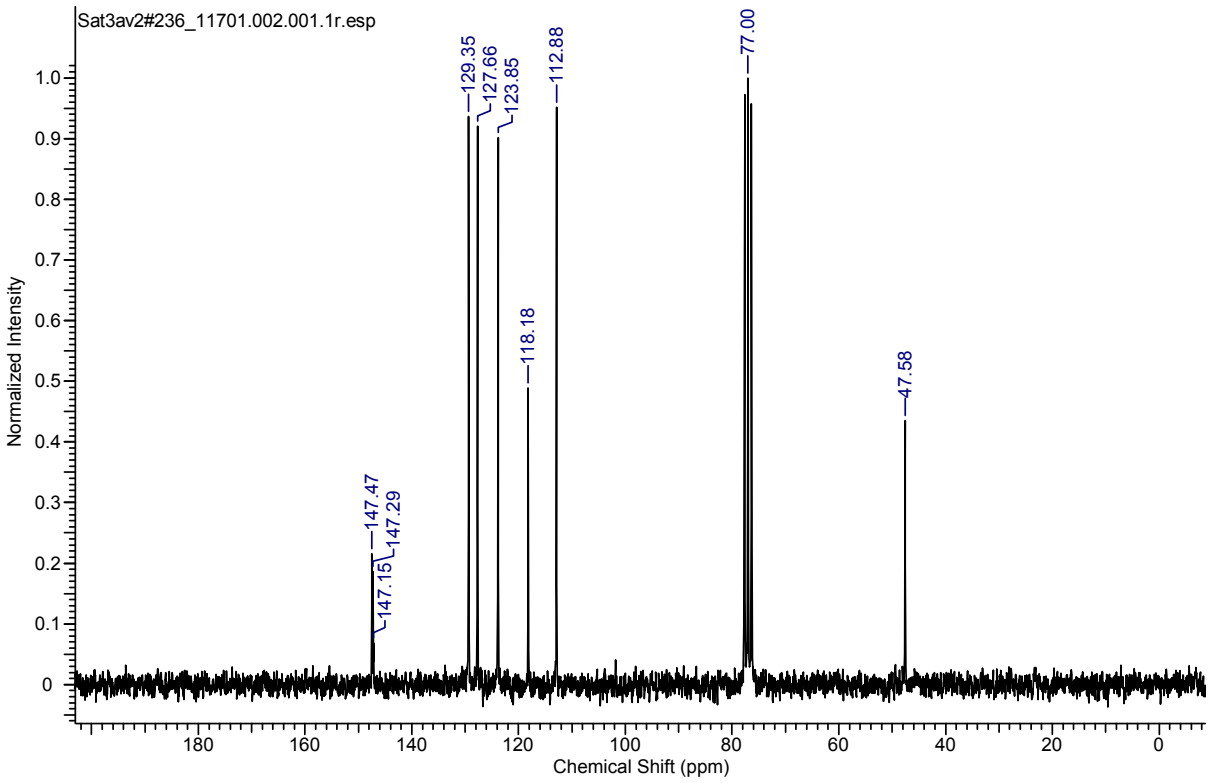
^{13}C NMR Spectrum of Isolated **N-(4-methylbenzyl)aniline (17)** ($CDCl_3$, 50.28 MHz, 298 K)



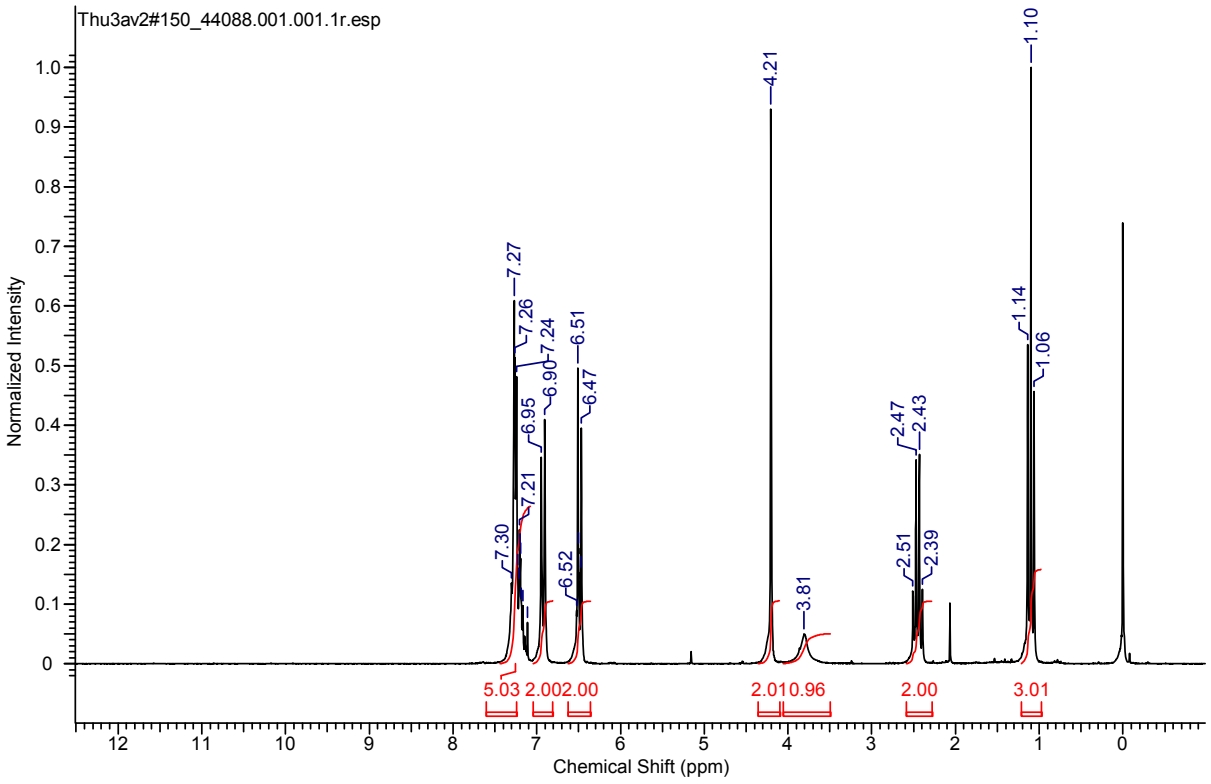
^{1}H NMR Spectrum of Isolated **N-(4-nitrobenzyl)aniline (18)** ($CDCl_3$, 200 MHz, 298 K)



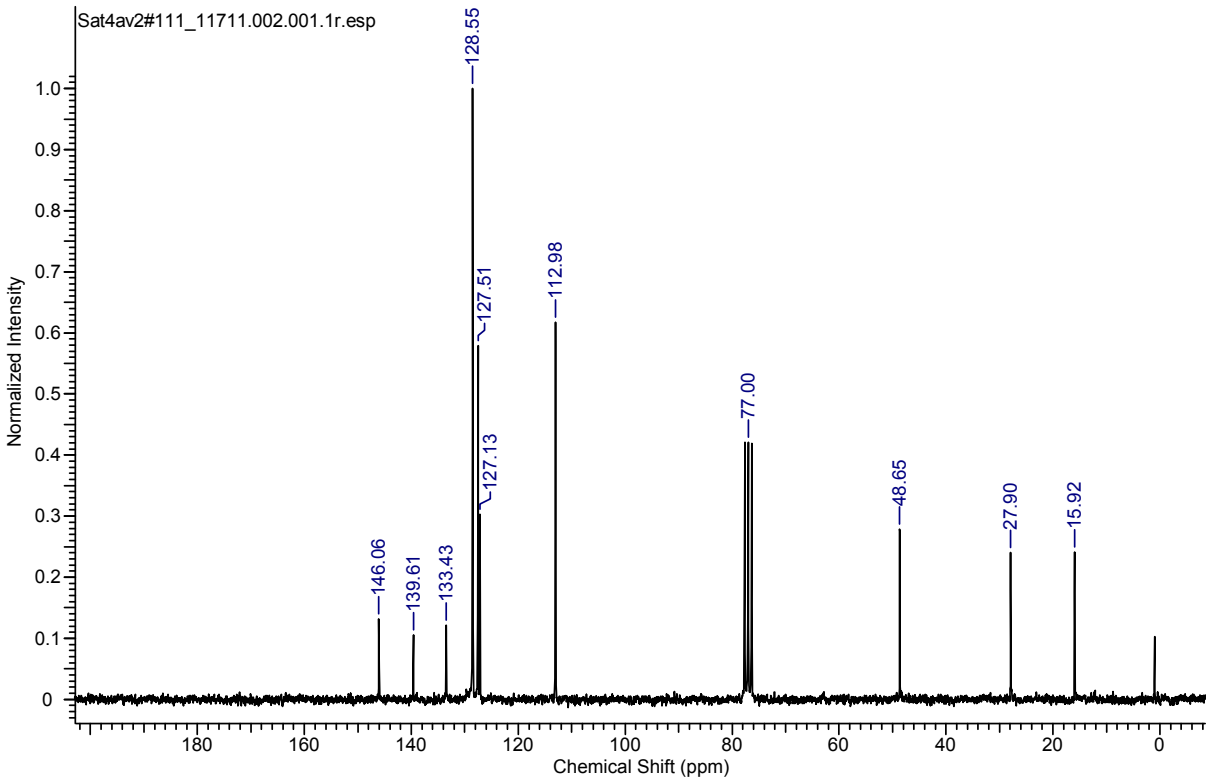
^{13}CNMR Spectrum of Isolated **N-(4-nitrobenzyl)aniline (18)** ($CDCl_3$, 50.28 MHz, 298 K)



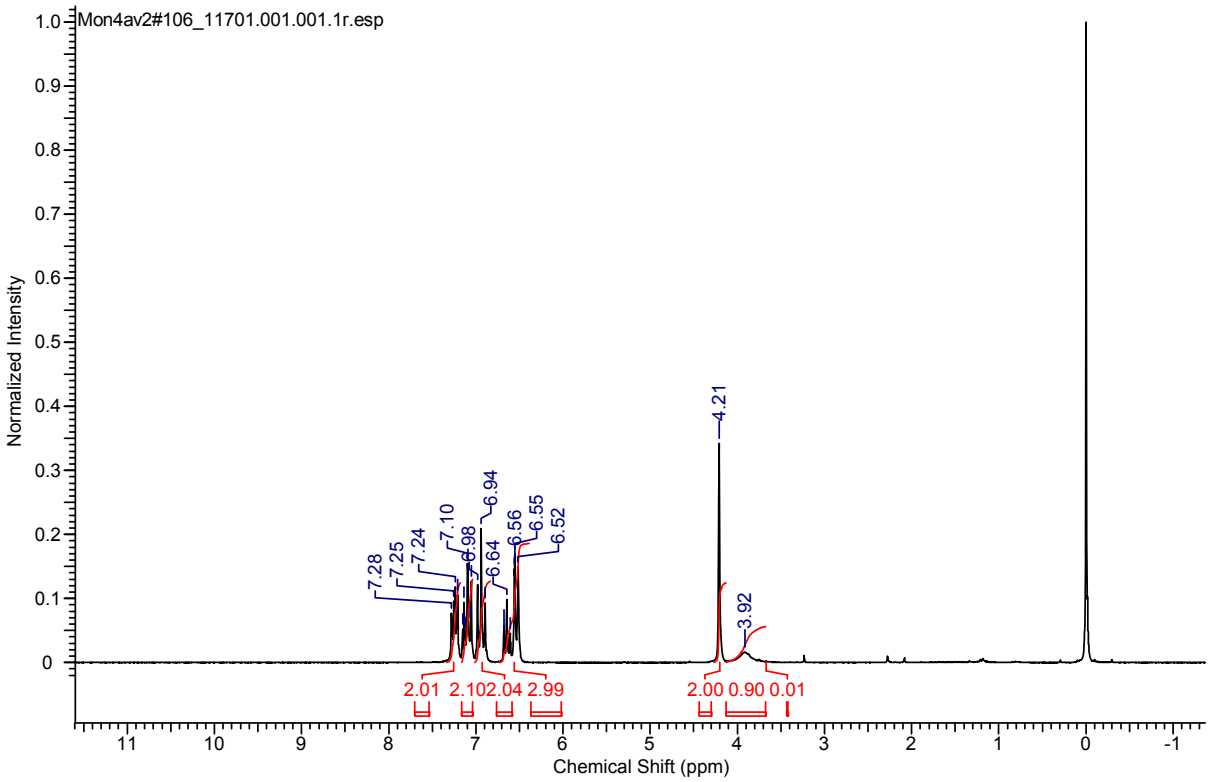
^{1}H NMR Spectrum of Isolated **N-benzyl-4-ethylaniline (19)** ($CDCl_3$, 200 MHz, 298 K)



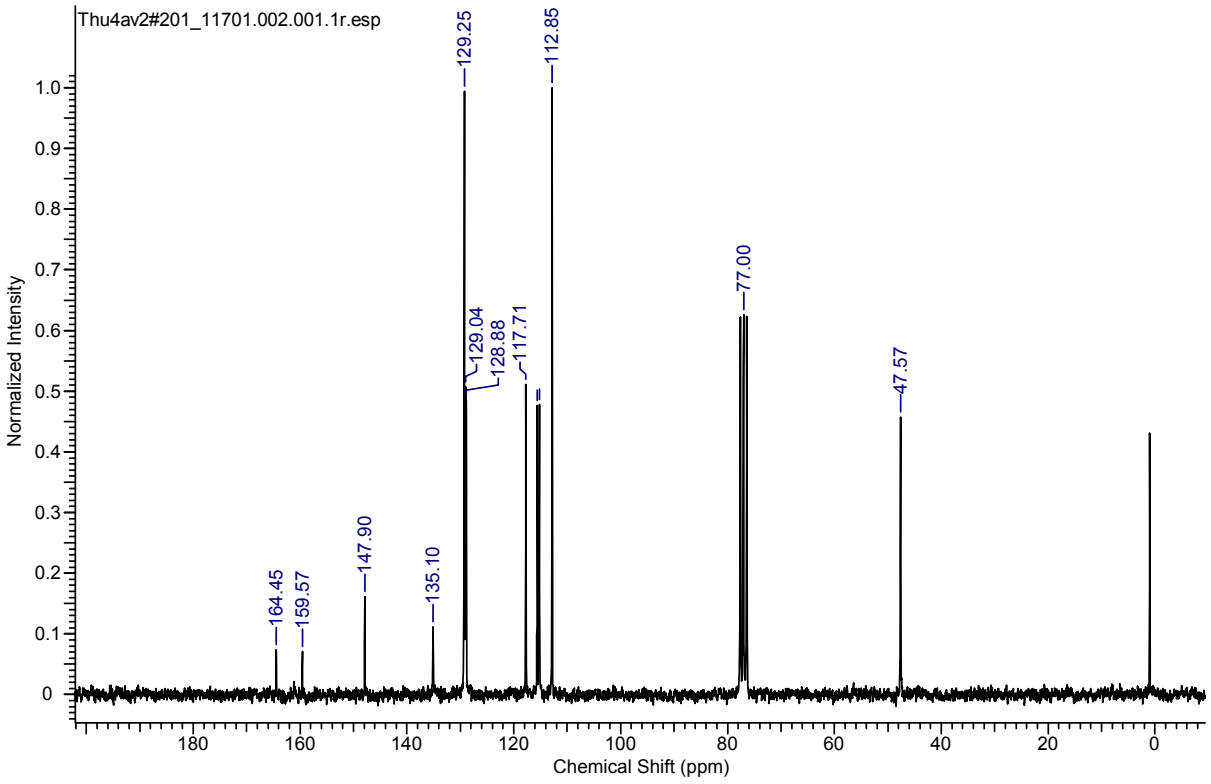
^{13}C NMR Spectrum of Isolated **N-benzyl-4-ethylaniline (19)** ($CDCl_3$, 50.28 MHz, 298 K)



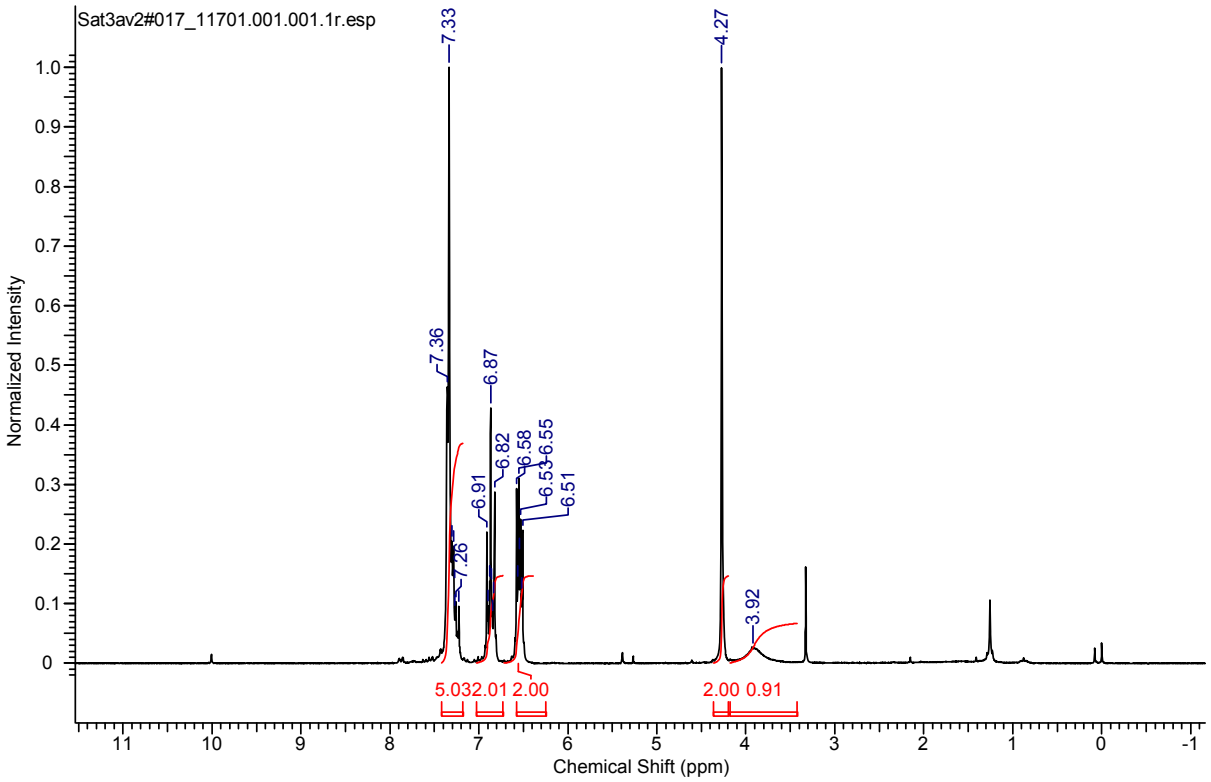
^{1}H NMR Spectrum of Isolated **N-(4-fluorobenzyl)aniline (20)** ($CDCl_3$, 200 MHz, 298 K)



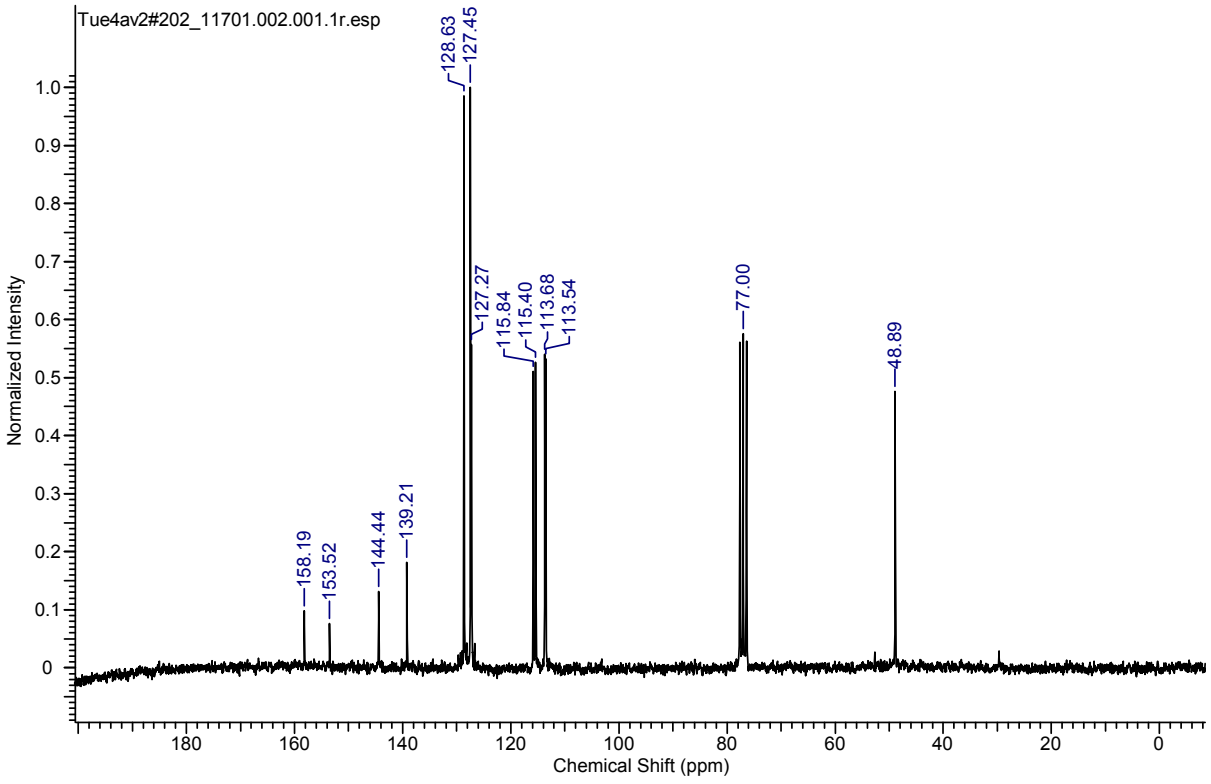
^{13}C NMR Spectrum of Isolated **N-(4-fluorobenzyl)aniline (20)** ($CDCl_3$, 50.28 MHz, 298 K)



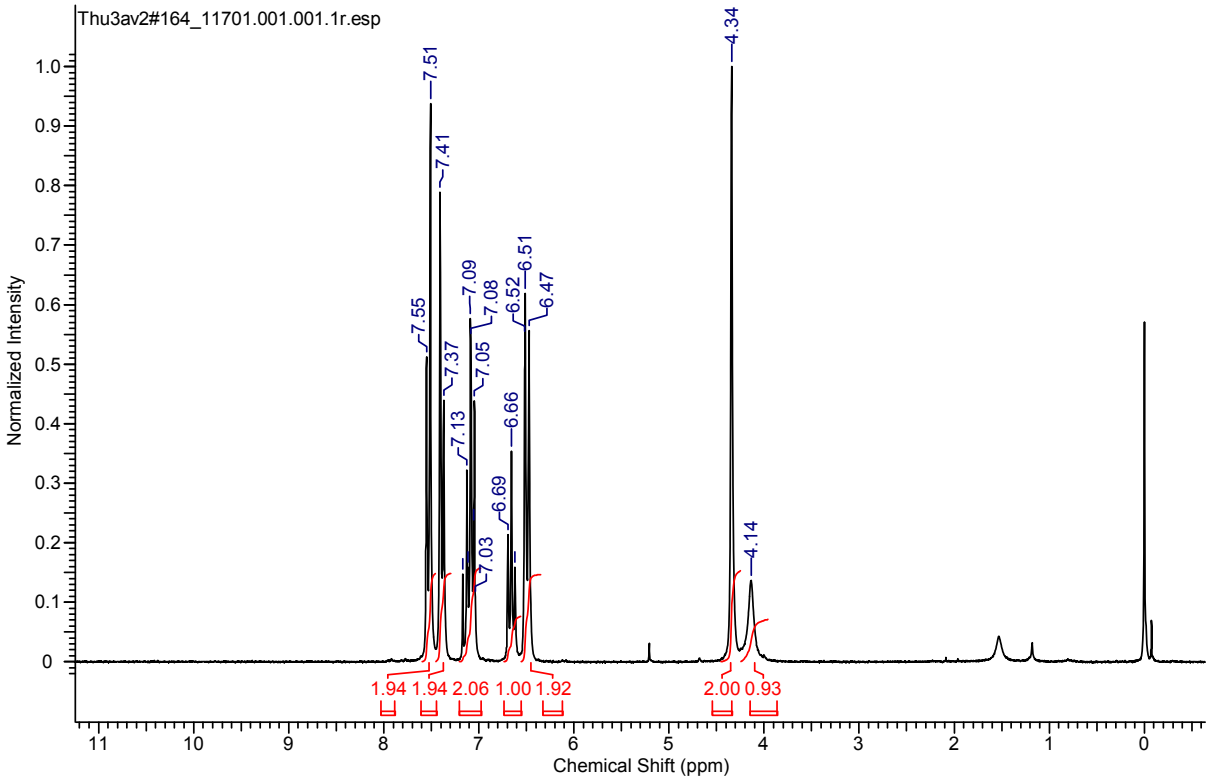
^{1}H NMR Spectrum of Isolated **N-benzyl-4-fluoroaniline (21)** ($CDCl_3$, 200 MHz, 298 K)



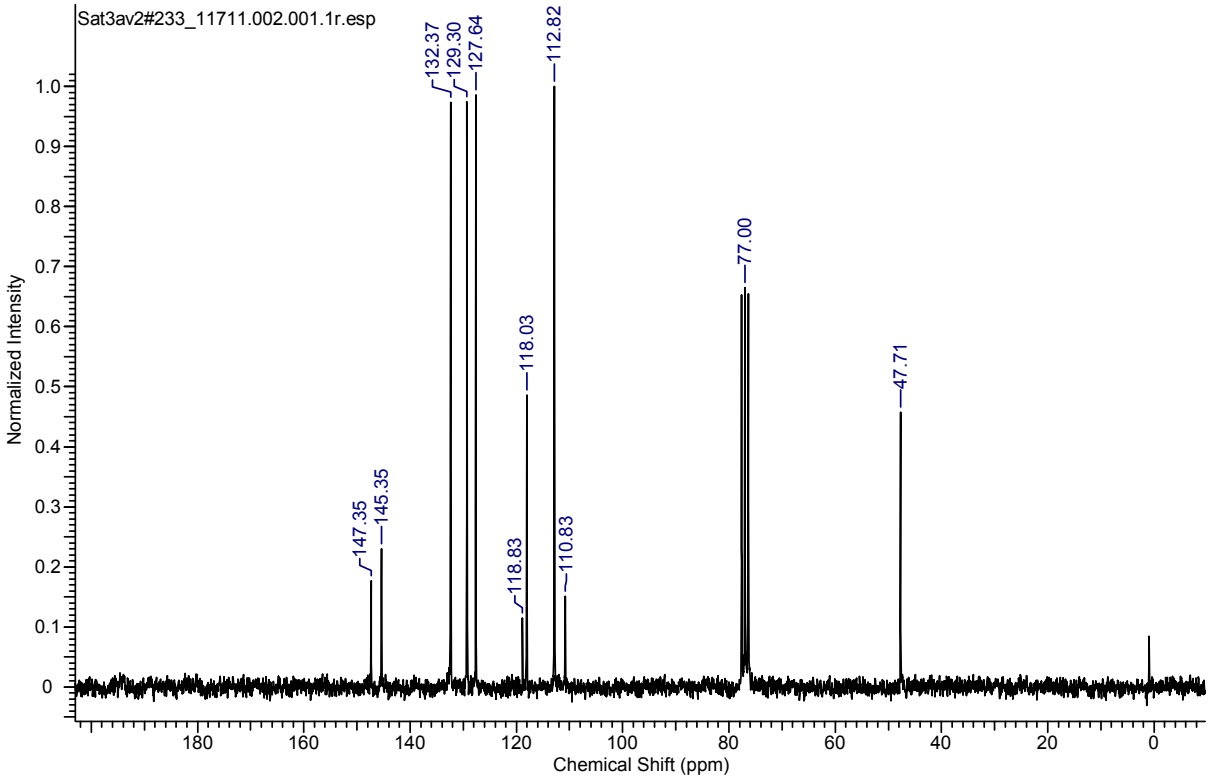
^{13}C NMR Spectrum of Isolated **N-benzyl-4-fluoroaniline (21)** ($CDCl_3$, 50.28 MHz, 298 K)



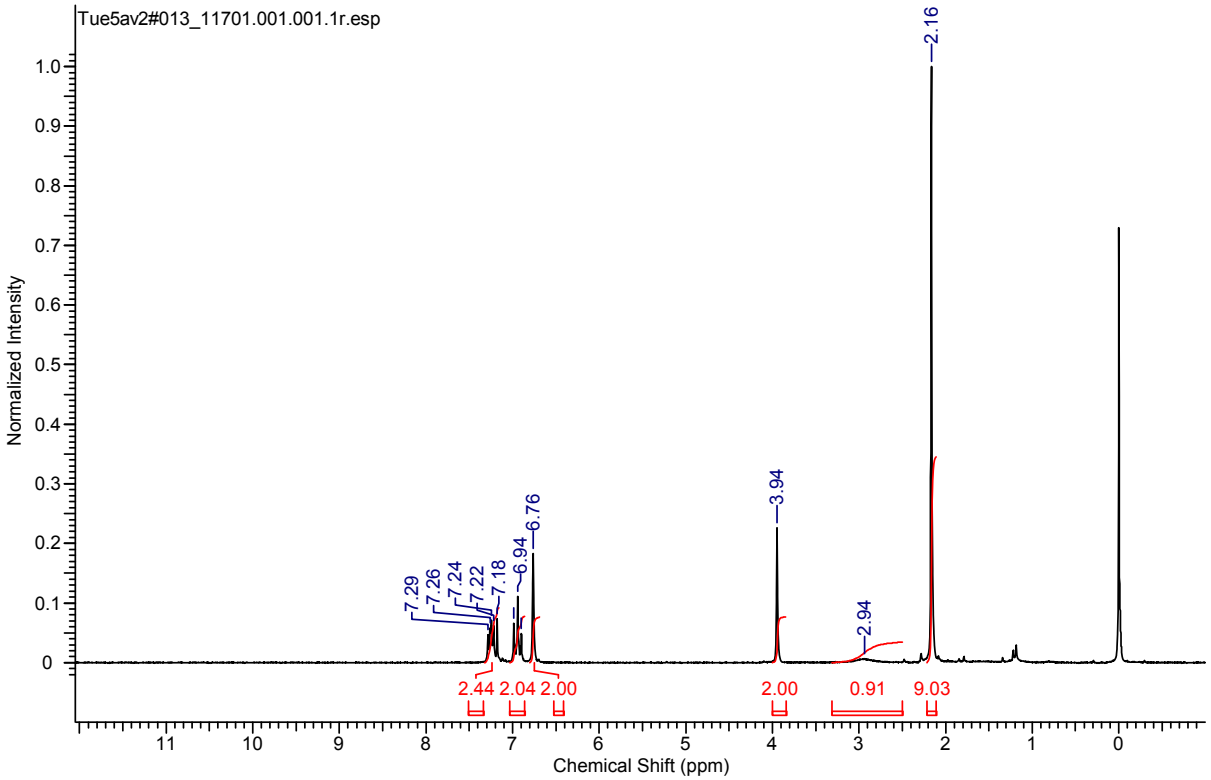
^{1}H NMR Spectrum of Isolated **4-((phenylamino)methyl)benzonitrile (22)** ($CDCl_3$, 200 MHz, 298 K)



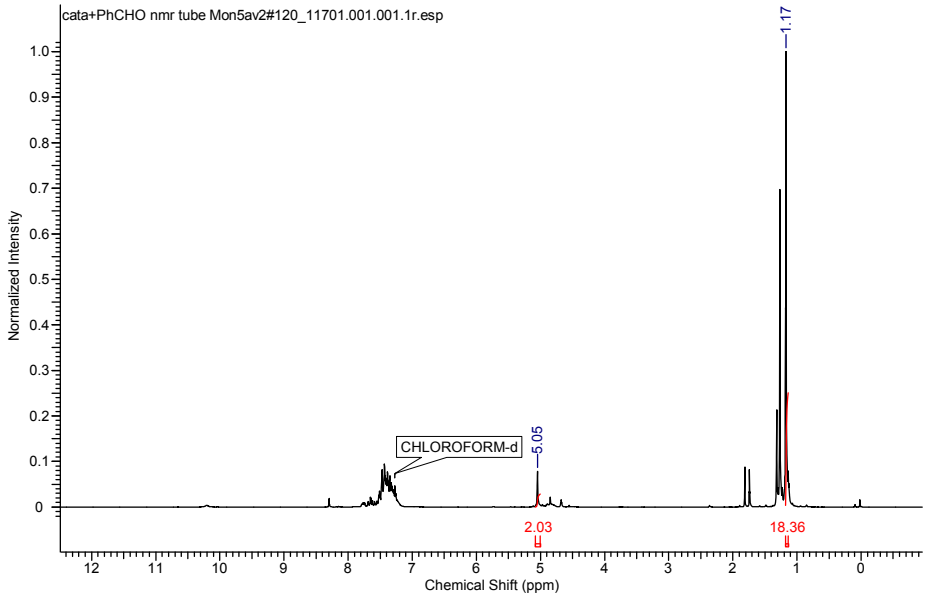
^{13}C NMR Spectrum of Isolated **4-((phenylamino)methyl)benzonitrile (22)** ($CDCl_3$, 50.28 MHz, 298 K)



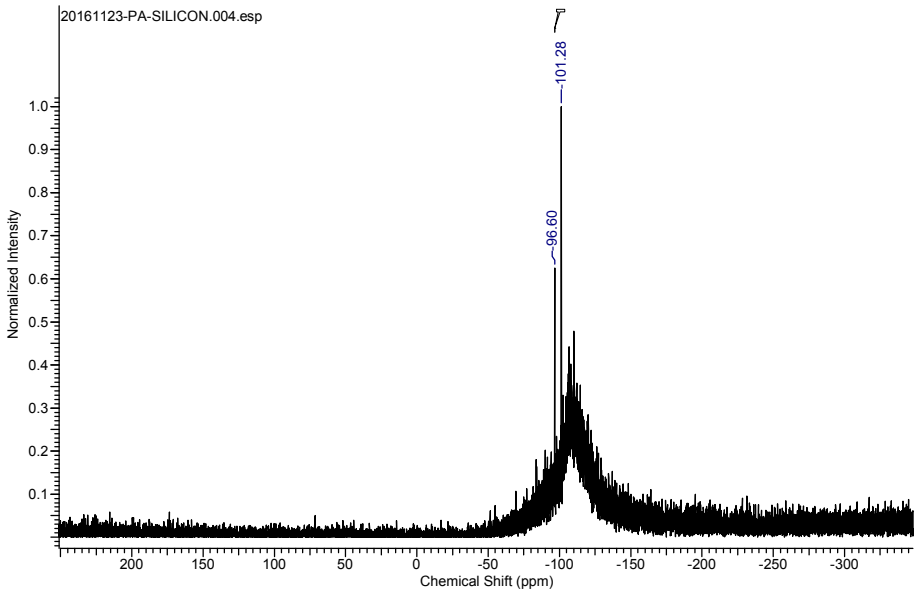
^{1}H NMR Spectrum of isolated **N-(4-fluorobenzyl)-2,4,6-trimethylaniline (23)** ($CDCl_3$, 200 MHz, 298 K)



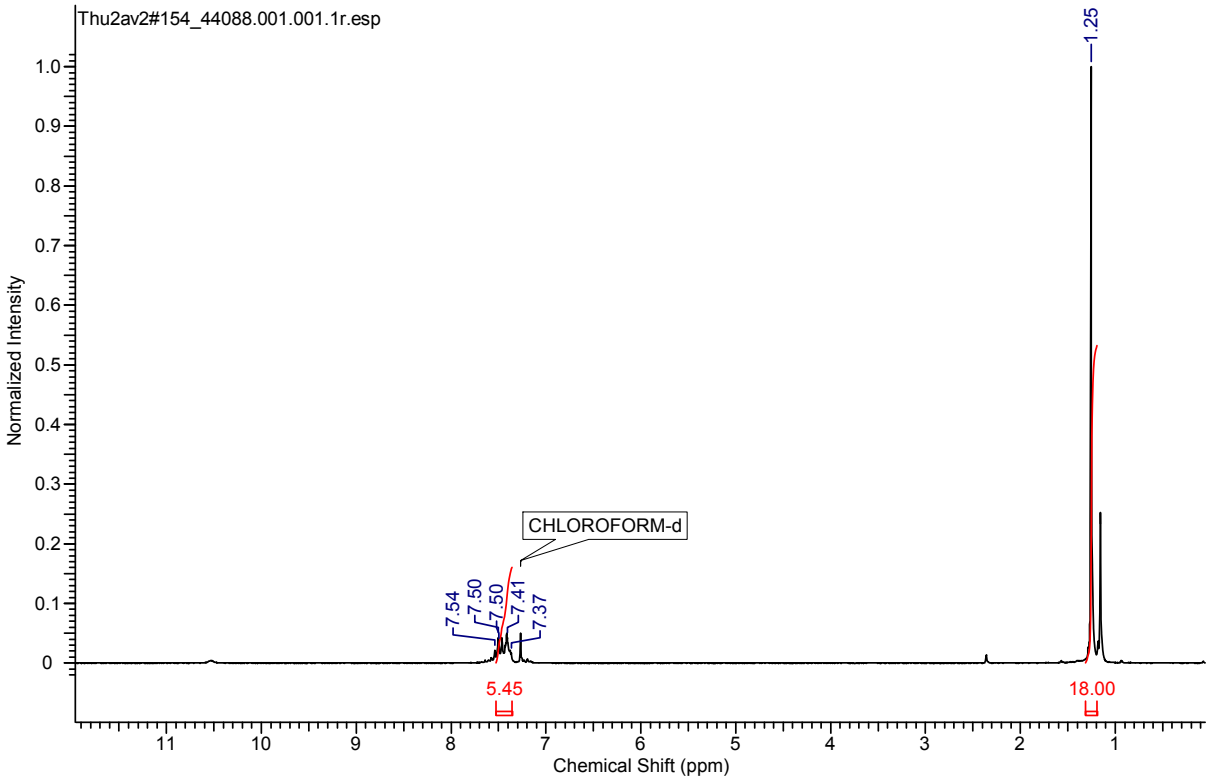
^{1}H NMR Spectrum of **Int-2** ($CDCl_3$, 200 MHz, 298 K)



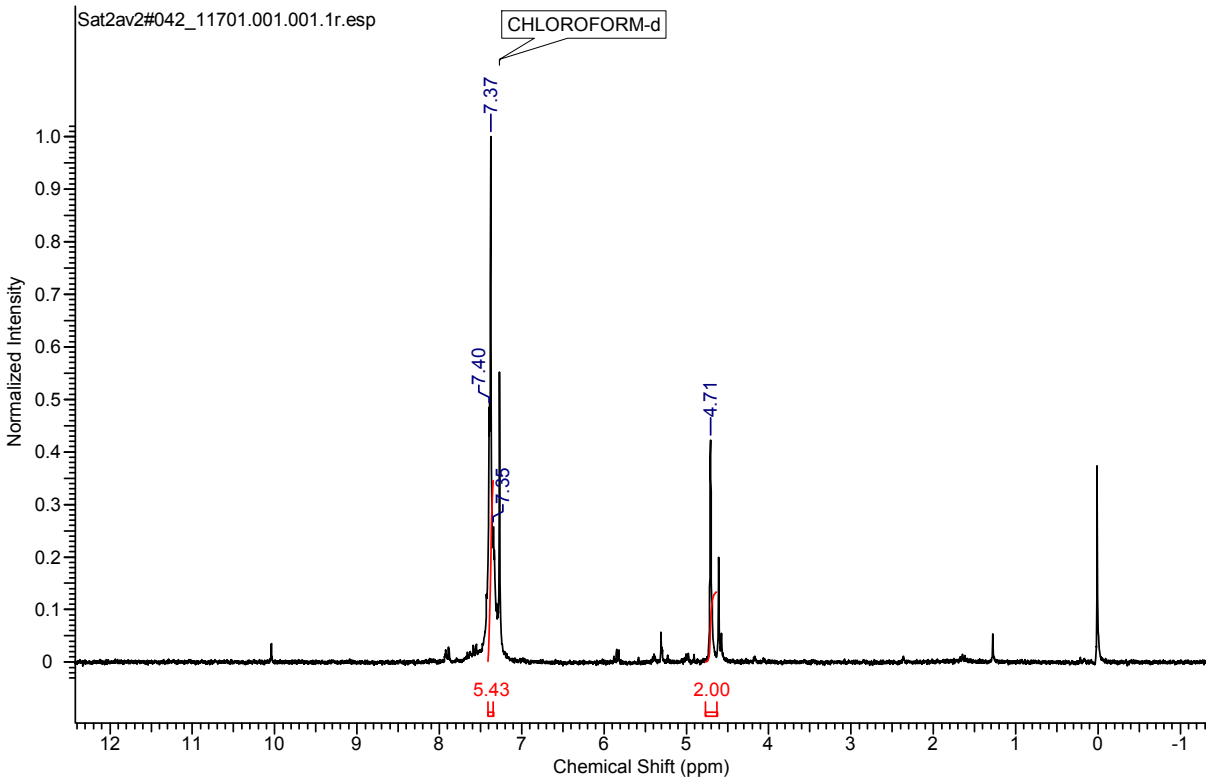
$^{29}Si\{^{1}H\}$ NMR Spectrum of **Int-2** ($CDCl_3$, 200 MHz, 298 K)



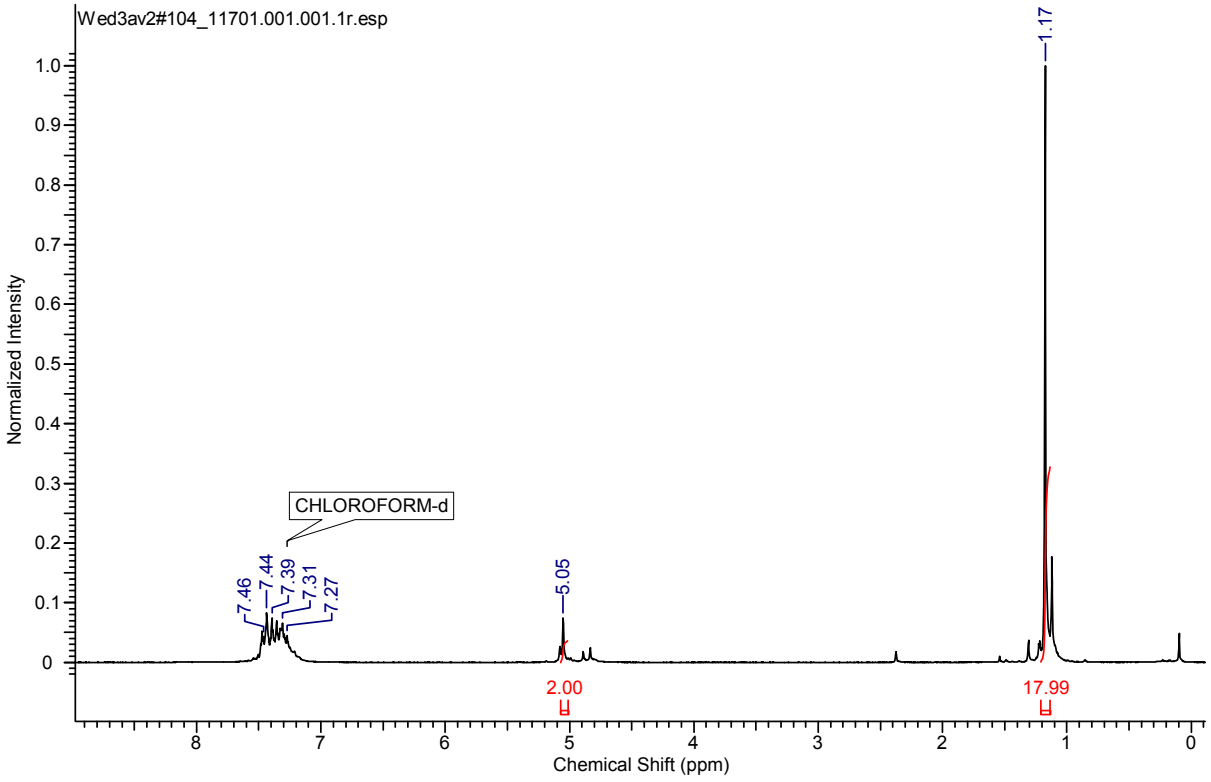
^{1}H NMR of $PhC(NtBu)_2SiCl_3$ ($CDCl_3$, 200MHz, 298K):



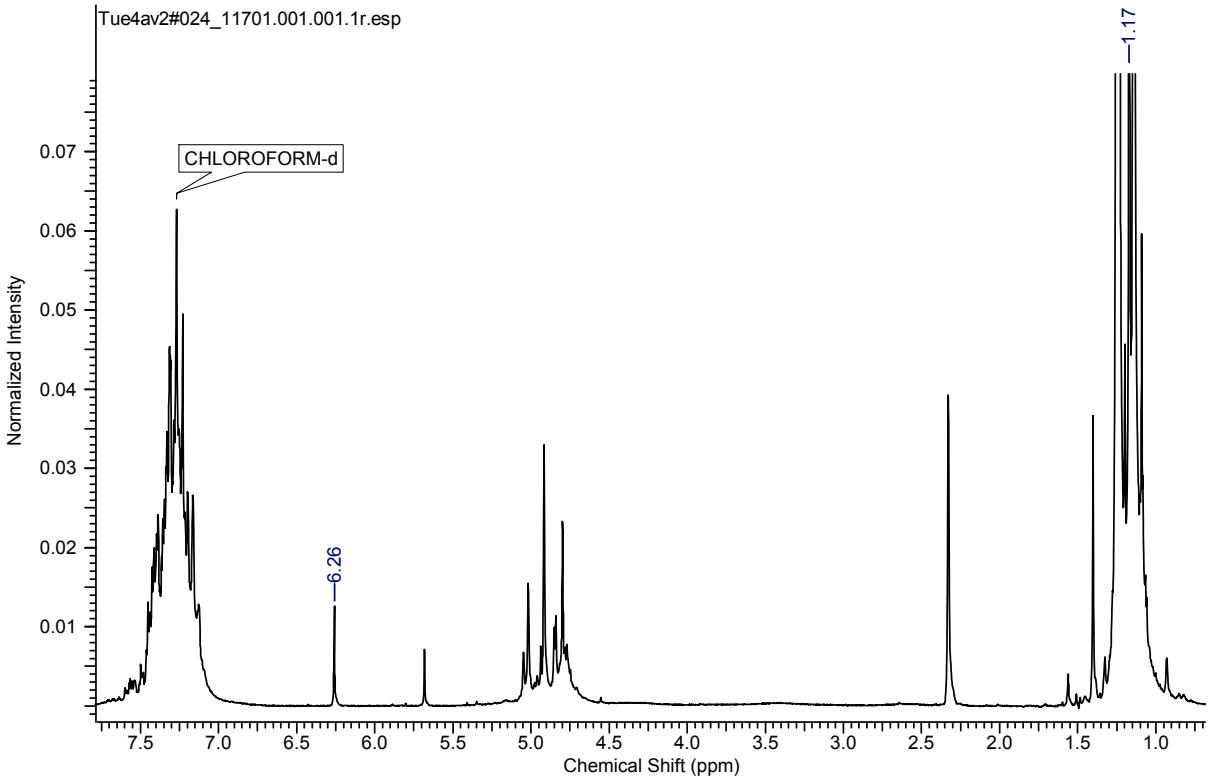
^{1}H NMR of BnOK($CDCl_3$, 200MHz, 298K):



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



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



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