Supplementary Information

for

Easily accessible lithium compounds catalyzed mild and facile hydroboration and cyanosilylation of aldehydes and ketones

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Contents:

General Experimental Information:

All reactions were performed under argon atmosphere using Schlenk techniques or inside a MBraun glove box. Catalysts **1a**, **1b** and **1c** were prepared by the previously reported methods.[S1-S3] Pinacolborane (HBpin), aldehydes and ketones were purchased from Sigma–Aldrich, TCI and used without further purification. THF was distilled from Na/benzophenone and further dried by molecular sieves prior to use. C_6D_6, toluene-d_8 and $CDCl_3$ were purchased from Sigma- Aldrich, were degassed by three freeze-pump-thaw cycles and stored over molecular sieves. ^1H, $^{13}C\{1H\}$ and ^{11}B NMR spectra were recorded on Bruker AV–200 MHz and AV-400 MHz, respectively and referenced to the resonances of the solvent used.

General catalytic procedure for the hydroboration of aldehydes:

Aldehyde (0.5 mmol), pinacolborane (0.5 mmol), 0.5 mL stock solution of catalyst (0.1 mol%) in THF were charged in a Schlenk tube with a magnetic bead inside the glove box. The reaction mixture was allowed to stir at room temperature for 60 min for **1a**, 40 min for **1b** and 50 min for **1c** respectivly. Upon completion of reaction, the solvent was removed using high vacuum in a Schlenk line and mesitylene (0.5 mmol) as internal standard, was added while making the NMR in $CDCl_3$.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.

Table S1a. Optimization Table of Hydroboration of Benzaldehyde Catalysed by 1a

Entry	Catalyst(mol%)	Time(min)	Solvent	NMR Yield(%)
1.	0.5	60	THF	98
2.	0.5	15	THF	97
3.	0.2	60	THF	94
4.	0.1	60	THF	91
5.	0.1	30	THF	71
6.	0.05	120	THF	76

Table S1b. Optimization Table of Hydroboration of Benzaldehyde Catalysed by 1b

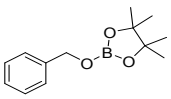
Entry	Catalyst(mol%)	Time(min)	Solvent	NMR Yield(%)
1.	0.5	30	THF	>99
2.	0.5	10	THF	99
3.	0.1	60	THF	>99
4.	0.1	40	THF	94
5.	0.1	30	THF	90
6.	0.05	120	THF	84

Table S1c. Optimization Table of Hydroboration of Benzaldehyde Catalysed by 1c

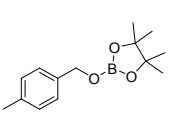
Entry	Catalyst(mol%)	Time(min)	Solvent	NMR Yield(%)
1.	0.5	30	THF	>99
2.	0.5	15	THF	96
3.	0.1	60	THF	96
4.	0.1	50	THF	90
5.	0.1	40	THF	82
6.	0.05	120	THF	81

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

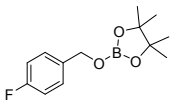
2-(benzyloxy)-pinacolborane (2a): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.28-7.18 (m, 5H, Ar*H*), 4.84 (s, 2H, OCH_2), 1.16 (s, 12H, CH_3) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 139.09 (Ar*C*-R), 128.11 (*Ph*), 127.20 (*Ph*), 126.57 (*Ph*), 82.75 (*C*(CH_3)$_2$), 66.51 (*C*H_2), 24.41(*C*H_3) ppm.



2-((4-methylbenzyl)oxy)-pinacolborane (2b): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.17-7.13 (d, $^{3}J_{H-H}$=8.08Hz, 2H, Ar*H*), 7.05-7.01 (d, $^{3}J_{H-H}$=7.96 Hz, 2H, Ar*H*), 4.80 (s, 2H, CH_2), 2.23 (s, 3H, ArCH_3), 1.16 (s, 12H, CH_3) ppm;^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 136.81 (*Ph*), 136.19 (*Ph*), 129.68 (*Ph*), 129.54 (*Ph*), 128.83 (*Ph*), 82.72 (*C*(CH_3)$_2$), 66.47 (*C*H_2), 24.46 (*C*H_3), 20.97 (Ar-*C*H_3) ppm.



2-((4-fluorobenzyl)oxy)-pinacolborane (2c): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.25-7.18 (t, 2H, Ar*H*), 6.95-6.86 (t, 2H, Ar*H*), 4.78 (s, 2H, CH_2), 1.17 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 162.09 (*d*,J_{C-F} = 245.17



Hz, Ar*C*-F), 134.88 (Ar-C), 128.50 (d, J_{C-F}=8.05 Hz, Ar-*C*), 114.96 (d, J_{C-F}=21.22 Hz, Ar-*C*), 82.87 (*C*(CH_3)$_2$), 65.91 (*C*H_2), 24.42 (*C*H_3) ppm.

2-(4-nitrobenzyloxy)-pinacolborane (2d): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 8.09 (d,$^3J_{H-H}$=8.59Hz, 2H, Ar*H*), 7.40 (d,$^3J_{H-H}$=8.46 Hz, 2H, Ar*H*), 4.93 (s, 2H, C*H*2), 1.20 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 147.02 (Ar*C*-NO_2), 146.43 (*Ph*), 123.33 (*Ph*), 83.16 (*C*(CH_3)$_2$), 65.34 (*C*H_2), 24.37 (*C*H_3) ppm.

2-(4-hydroxybenzyloxy)-pinacolborane (2e): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.09 (d,$^3J_{H-H}$=8.59 Hz, 2H, Ar*H*), 7.74-6.71 (m, 2H, Ar*H*), 4.75 (s, 2H, CH_2), 1.17 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 155.57 (Ar*C*-OH), 132.42 (*Ph*), 130.60 (*Ph*), 128.63 (*Ph*), 115.20 (*Ph*), 83.02 (*C*(CH_3)$_2$), 66.54 (*C*H_2), 24.36 (*C*H_3) ppm.

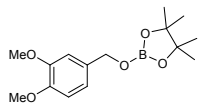
2-(2-hydroxybenzyloxy)-pinacolborane (2f): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.14-7.04 (m, 2H, Ar*H*), 6.79 (d,$^3J_{H-H}$=8.59 Hz, 2H, Ar*H*), 4.89 (s, 2H, CH_2), 1.17 (s,12H,CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 154.87 (Ar*C*-OH), 129.41 (*Ph*), 124.19 (*Ph*), 120.15 (*Ph*), 116.73 (*Ph*), 83.44 (*C*(CH_3)$_2$), 64.36 (*C*H_2), 24.35 (*C*H_3) ppm.

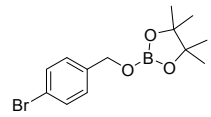
2-(4-cyanobenzyloxy)-pinacolborane (2g): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.51 (d, $^3J_{H-H}$=7.71 Hz, 2H, Ar*H*), 7.33 (d, $^3J_{H-H}$=7.58 Hz, 2H, Ar*H*), 4.88 (s, 2H, CH_2), 1.18 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 144.37 (*Ph*), 131.88 (*Ph*), 126.61 (*Ph*), 118.56 (Ar-*C*N), 110.88 (Ar*C*-CN), 83.04 (*C*(CH_3)$_2$), 65.50 (*C*H_2), 24.34 (*C*H_3) ppm;^{11}B NMR (C_6D_6, 128 MHz, 298 K): δ 22.78 ppm.

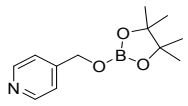
2-((2-methoxybenzyl)oxy)-pinacolborane (2h): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.33 (d, $^3J_{H-H}$=7.45 Hz, 1H, Ar*H*), 7.13 (t, 1H, Ar*H*), 6.85 (t, 1H, Ar*H*), 6.73 (s, 1H, Ar*H*), 4.91 (s, 2H, CH_2), 3.67 (s, 3H, OCH_3), 1.17 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 156.32 (Ar*C*-OMe), 128.05 (*Ph*), 127.54 (*Ph*), 127.12 (*Ph*), 120.15 (*Ph*), 109.60 (*Ph*), 82.59 (*C*(CH_3)$_2$), 62.08 (*C*H_2), 54.87 (*Ar*-O*C*H_3), 24.40 (*C*H_3) ppm.

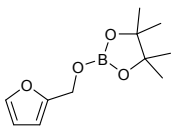
2-(naphthalen-1-ylmethoxy)-pinacolborane (2i): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.97-7.92 (m,1H,Ar*H*), 7.75-7.68 (m, 2H, Ar*H*), 7.53-7.49 (m, 1H, Ar*H*), 7.40-7.33 (m, 2H, Ar*H*), 5.33 (s, 2H, CH_2), 1.17(s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 136.38 (*Ph*), 134.93(*Ph*), 130.8 (*Ph*),

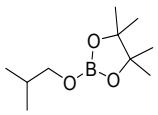
128.37 (*Ph*), 128.00 (*Ph*), 125.89 (*Ph*), 125.45 (*Ph*), 125.14 (*Ph*), 124.69 (*Ph*), 123.26 (*Ph*), 82.76 (*C*$(CH_3)_2$), 64.83 (*C*H_2), 24.39 (*C*H_3) ppm.

2-((3,4-dimethoxybenzyl)oxy)-pinacolborane (2j): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 
6.85-6.77 (m, 2H, Ar*H*), 6.72 (s, 1H, Ar*H*), 4.77 (s, 2H, CH_2), 3.77 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 1.17 (s, 12H, CH_3) ppm; ^{13}C NMR (CDCl3, 50.28 MHz, 298 K): δ 148.70 (Ar*C*-OMe), 148.22 (Ar*C*-OMe), 131.70 (*Ph*), 119.17 (*Ph*), 110.70 (*Ph*), 110.22 (*Ph*), 82.62 (*C*$(CH_3)_2$), 66.41 (*C*H_2), 55.59 (-O*C*H_3), 55.48 (-O*C*H_3), 24.35 (*C*H_3) ppm; ^{11}B NMR (C_6D_6, 128 MHz, 298 K): δ 22.90 ppm.

2-((4-bromobenzyl)oxy)-pinacolborane (2k): ^{1}H NMR ($CDCl_3$, 200MHz, 298 K): δ 7.34 
(d, $^3J_{H-H}$=8.34 Hz, 2H, Ar*H*), 7.11 (d, $^3J_{H-H}$=8.34 Hz, 2H, Ar*H*), 4.77 (s, 2H, CH_2), 1.16 (s, 12H, CH_3) ppm;^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 138.07 (*Ph*), 131.21 (*Ph*), 128.25 (*Ph*), 121.01 (Ar-Br), 82.91 (*C*$(CH_3)_2$), 65.79 (*C*H_2), 24.40(*C*H_3) ppm.

4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)pyridine (2l): ^{1}H NMR 
($CDCl_3$, 200 MHz, 298 K): δ 8.48 (d, $^3J_{H-H}$=5.81 Hz, 2H, Ar*H*), 7.16 (d,$^3J_{H-H}$=5.43 Hz, 2H, Ar*H*), 4.84 (s, 2H, CH_2), 1.18 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 149.03 (*Ar*), 148.17 (*Ar*), 120.55 (*Ar*), 82.74 (*C*$(CH_3)_2$), 64.47 (*C*H_2), 24.17 (*C*H_3) ppm.

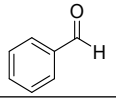
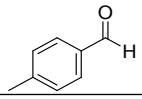
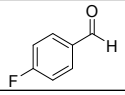
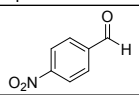
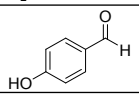
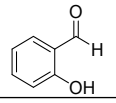
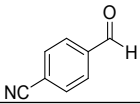
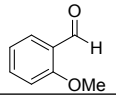
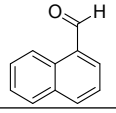
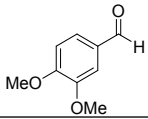
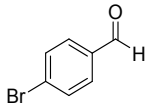
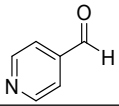
2-(furan-2-ylmethoxy)-pinacolborane (2m): ^{1}HNMR ($CDCl_3$, 200 MHz, 298 K): δ 7.25 (t, 
$^3J_{H-H}$=2.65 Hz, 1H, Ar*H*), 6.70 (s, 2H, Ar*H*), 4.73 (s, 2H, CH_2), 1.16 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 152.33 (*Ar*), 142.15 (*Ar*), 110.01 (*Ar*), 108.02 (*Ar*), 82.75 (*C*$(CH_3)_2$), 58.94 (*C*H_2), 24.30 (*C*H_3) ppm.

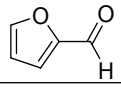
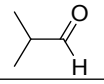
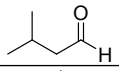
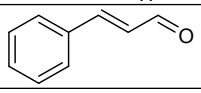
2-isobutoxy-pinacolborane (2n): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 3.53 (d, $^3J_{H-H}$=6.44 
Hz, 2H, CH_2), 1.73 (sept, 1H, C*H*$(CH_3)_2$), 1.16 (s, 12H, CH_3), 0.81 (d, $^3J_{H-H}$=6.69 Hz, 6H, CH(CH_3)$_2$) ppm;^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 82.42 (*C*$(CH_3)_2$), 71.25 (*C*H_2), 29.74 (*C*H$(CH_3)_2$, 24.45 (*C*H_3), 21.05 (*C*H_3), 18.63 (*C*H_3) ppm.

2-(isopentyloxy)-pinacolborane (2o): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 3.79 (t, $^3J_{H-H}$=13.14 Hz, 2H, CH_2), 1.74-1.51 (m, 1H, CH_2C*H*$(CH_3)_2$, 1.37 (q, 2H, CH_2), 1.16 (s, 12H, CH_3), 0.82 (d, $^3J_{H-H}$=7.51 Hz, 6H, CH(CH_3)$_2$) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 82.46 (*C*$(CH_3)_2$), 63.23 (*C*H_2), 40.25, 24.4 (*C*H$(CH_3)_2$, 24.42 (*C*H_3), 21.08 (*C*H_3) ppm.

2-(cinnamyloxy)-pinacolborane (2p): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.29-7.14 (m, 5H, Ar*H*), 6.57-6.50 (d, 1H, $^{3}J_{H\text{-}H}$=15.79 Hz, 1H ArC*H*), 6.25-6.12 (m, 1H, CHC*H*), 4.46-4.43 (d, 2H, $^{3}J_{H\text{-}H}$=6.1 Hz, CH_2), 1.17 (s, 12H, CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 136.68 (Ar*C*-R), 130.46 (Ar-CH*C*H), 128.31 (Ar-*C*H), 127.29 (*Ph*), 126.61 (*Ph*), 126.23 (*Ph*), 82.65 (*C*(CH_3)$_2$), 65.05 (*C*H_2), 24.38 (*C*H_3) ppm.

Table S2. TOF(h^{-1}) for aldehyde hydroboration

Entry	Substrate	NMR Yield(%)	TOF(h^{-1})
2a		91[a]/94[b]/90[c]	910[a]/705[b]/1080[c]
2b		80[a]/98[b]/52[c]	800[a]/735[b]/624[c]
2c		78[a]/99[b]/60[c]	780[a]/743[b]/720[c]
2d		96[a]/99[b]/97[c]	960[a]/743[b]/1164[c]
2e		74[a]/80[b]/83[c]	740[a]/600[b]/996[c]
2f		71[a]/71[b]/73[c]	710[a]/533[b]/876[c]
2g		99[a]/>99[b]/>99[c]	990[a]/>743[b]/>1188[c]
2h		98[a]/>99[b]/>99[c]	980[a]/>743[b]/>1188[c]
2i		82[a]/67[b]/85[c]	820[a]/503[b]/1020[c]
2j		>99[a]/99[b]/>99[c]	>990[a]/743[b]/>1188[c]
2k		97[a]/98[b]/99[c]	910[a]/735[b]/1188[c]
2l		92[a]/94[b]/92[c]	920[a]/705[b]/1104[c]

2m		95[a]/98[b]/99[c]	950[a]/735[b]/1188[c]
2n		94[a]/96[b]/96[c]	940[a]/720[b]/1152[c]
2o		92[a]/82[b]/92[c]	920[a]/615[b]/1104[c]
2p[d]		64 [a]/90 [b]/65 [c]	128[a]/90[b]/130[c]

Reaction conditions: Catalyst: 0.1 mol% , Reaction conditions: room temperature in THF. Reaction time (except *trans*-cinnamaldehyde): **1a**: 60 min, **1b**: 40 min, **1c**: 50 min. Yields are calculated w.r.t. mesitylene as internal standard. Superscripts a, b and c stand forthe catalyst **1a**, **1b** and **1c**, respectively; [d]the reaction time for *trans*-cinnamaldehyde reduction was 5 h.TOF(h^{-1}) are calculated per active site in catalysts.

General catalytic procedure for the hydroboration of ketones:

Ketones (0.5 mmol), pinacolborane (0.5 mmol), 0.5 mL stock solution of catalyst (0.1 mol%) in THF were charged in a Schlenk tube with a magnetic bead inside the glove box. The reaction mixture was allowed to stir at room temperature for 3h for **1a** and 2h for **1b** and **1c**. Upon completion of reaction, the solvent was removed using high vacuum in a Schlenk line and mesitylene (0.5 mmol) as internal standard, was added while making the NMR in $CDCl_3$.The progress of the reaction was monitored by ^1H NMR, which indicated the completion of the reaction by appearance of a new C*H* resonance.

Table S3a. Optimization Table of Hydroboration of Acetophenone Catalysed by 1a

Entry	Catalyst(mol%)	Time(h)	Solvent	NMR Yield(%)
1.	0.5	3	THF	99
2.	0.4	2	THF	99
3.	0.3	2	THF	98
4.	0.2	3	THF	99
5.	0.1	3	THF	94
6.	0.1	2.5	THF	71

Table S3b. Optimization Table of Hydroboration of Acetophenone Catalysed by 1b

Entry	Catalyst(mol%)	Time(h)	Solvent	NMR Yield(%)
1.	0.5	3	THF	>99
2.	0.4	2	THF	>99
3.	0.2	2	THF	98

4.	0.1	2.25	THF	96
5.	0.1	2	THF	95
6.	0.1	1.5	THF	73

Table S3c. Optimization Table of Hydroboration of Acetophenone Catalysed by 1c in THF

Entry	Catalyst(mol%)	Time(h)	Solvent	NMR Yield(%)
1.	0.5	3	THF	>99
2.	0.4	2	THF	>99
3.	0.2	2	THF	>99
4.	0.1	2.25	THF	98
5.	0.1	2	THF	98
6.	0.1	1.5	THF	69

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

2-(1-phenylethoxy)-pinacolborane (3a): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.31-7.12 (m, 5H, Ar*H*), 5.17 (q, 1H, BpinOC*H*), 1.41 (d, $^{3}J_{H\text{-}H}$=6.44 Hz, 3H, OCHCH_3), 1.14 (s, 6H, C(CH_3)$_2$), 1.11 (s, 6H, C(CH_3)$_2$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 144.43 (Ar*C*-R), 128.01 (*Ph*), 126.93 (*Ph*), 125.14 (*Ph*), 82.48 (*C*(CH$_3$)$_2$), 72.41 (O*C*HCH$_3$), 25.26 (OCH*C*H$_3$), 24.35 (C(*C*H$_3$)$_2$) ppm.

2-(1-(p-tolyl)ethoxy)-pinacolborane (3b): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.17 (d, $^{3}J_{H\text{-}H}$=8.08 Hz, 2H, Ar*H*), 7.02 (d, $^{3}J_{H\text{-}H}$=7.96 Hz, 2H, Ar*H*), 5.15 (q, 1H, BpinOC*H*), 2.22 (s, 3H, Ar-CH_3), 1.40 (d, $^{3}J_{H\text{-}H}$=6.44 Hz, 3H, OCHCH_3), 1.14 (s, 6H, C(CH_3)$_2$), 1.11 (s, 6H, C(CH_3)$_2$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 141.57 (Ar*C*-R), 136.50 (*Ph*), 128.57 (*Ph*), 125.20 (*Ph*), 82.55 (*C*(CH$_3$)$_2$), 72.35 (O*C*HCH$_3$), 25.34 (OCH*C*H$_3$), 24.44 (C(*C*H$_3$)$_2$), 21.08 (Ar-*C*H$_3$) ppm.

2-(1-(4-fluorophenyl)ethoxy)-pinacolborane (3c): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.27-7.20 (m, 2H, Ar*H*), 6.93-6.85 (m, 2H, Ar*H*), 5.14 (q, 1H, BpinOC*H*), 1.38 (d, $^{3}J_{H\text{-}H}$=6.44 Hz, 3H, OCHCH_3), 1.14 (s, 6H, C(CH_3)$_2$), 1.12 (s, 6H, C(CH_3)$_2$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 161.87 (*d*, $J_{C\text{-}F}$ = 244.43

Hz, Ar*C*-F), 140.31 (*Ph*), 127.01 (*Ph*), 114.84 (d, $J_{C\text{-}F}$=21.22 Hz, Ar-*C*), 82.68 (*C*(CH_3)$_2$), 71.92 (O*C*HCH$_3$), 25.29 (OCH*C*H$_3$), 24.43 (C(*C*H$_3$)$_2$), 24.37 (C(*C*H$_3$)$_2$) ppm.

2-(1-(4-methoxyphenyl)ethoxy)-pinacolborane (3d): ^{1}H NMR (CDCl$_3$, 200 MHz, 298 K): *δ* 7.20 (d, $^3J_{H\text{-}H}$=8.59 Hz, 2H, Ar*H*), 6.75 (d, $^3J_{H\text{-}H}$=8.72 Hz, 2H, Ar*H*), 5.14 (q, 1H, BpinOC*H*), 3.66 (s, 3H, -OC*H*$_3$), 1.39 (d, $^3J_{H\text{-}H}$=6.44 Hz, 3H, OCHC*H*$_3$), 1.14 (s, 6H, C(C*H*$_3$)$_2$), 1.12 (s, 6H, C(C*H*$_3$)$_2$) ppm; ^{13}C{1H} NMR (CDCl$_3$, 50.28 MHz, 298 K): *δ* 158.61 (Ar*C*-OMe), 136.64 (*Ph*), 126.45 (*Ph*), 113.38 (*Ph*), 82.46 (*C*(CH_3)$_2$), 72.07 (O*C*HCH$_3$), 54.93 (Ar-O*C*H3), 25.15 (OCH*C*H$_3$), 24.38 (C(*C*H$_3$)$_2$), 24.32 (C(*C*H$_3$)$_2$) ppm.

2-(1-(4-bromophenyl)ethoxy)-pinacolborane (3e): ^{1}H NMR (CDCl$_3$, 200 MHz, 298 K): *δ* 7.33 (d, $^3J_{H\text{-}H}$=8.46 Hz, 2H, Ar*H*), 7.13 (d, $^3J_{H\text{-}H}$=8.46 Hz, 2H, Ar*H*), 5.12 (q, 1H, BpinOC*H*), 1.37 (d, $^3J_{H\text{-}H}$=6.44 Hz, 3H, OCHC*H*$_3$), 1.14 (s, 6H, C(C*H*$_3$)$_2$), 1.11 (s, 6H, C(C*H*$_3$)$_2$) ppm; ^{13}C{1H} NMR (CDCl$_3$, 50.28 MHz, 298 K): *δ* 143.40 (Ar*C*-R), 131.05 (*Ph*), 126.89 (*Ph*), 120.63 (Ar*C*-Br), 82.55 (*C*(CH_3)$_2$), 71.72 (O*C*HCH$_3$), 54.93 (Ar-O*C*H3), 25.05 (OCH*C*H$_3$), 24.26 (C(*C*H$_3$)$_2$) ppm; ^{11}B NMR (C_6D_6, 128 MHz, 298 K): *δ* 22.57 ppm.

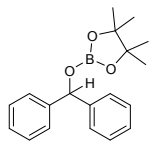
2-(1-(3-nitrophenyl)ethoxy)-pinacolborane (3f): ^{1}H NMR (CDCl$_3$, 200 MHz, 298 K): *δ* 8.16 (s, 1H, Ar*H*), 7.99 (d, $^3J_{H\text{-}H}$= 8.08 Hz, 1H, Ar*H*), 7.60 (d, $^3J_{H\text{-}H}$= 7.71 Hz, 1H, Ar*H*), 7.38 (t, 1H, Ar*H*), 5.25 (q, 1H, BpinOC*H*), 1.44 (d, $^3J_{H\text{-}H}$=6.44 Hz, 3H, OCHC*H*$_3$), 1.18 (s, 6H, C(C*H*$_3$)$_2$), 1.15 (s, 6H, C(C*H*$_3$)$_2$) ppm; ^{13}C{1H} NMR (CDCl$_3$, 50.28 MHz, 298 K): *δ* 148.06 (Ar*C*-NO$_2$), 146.43 (Ar*C*-R), 131.29 (*Ph*), 129.04 (*Ph*), 121.93 (*Ph*), 120.27 (*Ph*), 82.88 (*C*(CH_3)$_2$), 71.44 (O*C*HCH$_3$), 24.93 (OCH*C*H$_3$), 24.28 (C(*C*H$_3$)$_2$) ppm.

2-(1-(4-aminophenyl)ethoxy)-pinacolborane (3g): H NMR (CDCl$_3$, 200 MHz, 298 K): *δ* 7.03 (s, 2H, Ar*H*), 6.48 (s, 2H, Ar*H*), 5.08 (q, 1H, BpinOC*H*), 3.50 (s, 2H, Ar-NH$_2$), 1.38 (d, $^3J_{H\text{-}H}$= 6.44 Hz, 3H, OCHC*H*$_3$), 1.12 (s, 12H, C(C*H*$_3$)$_2$) ppm; ^{13}C{1H} NMR (CDCl$_3$, 50.28 MHz, 298 K): *δ* 145.48 (Ar*C*-NH$_2$), 134.25 (Ar*C*-R), 126.32 (*Ph*), 114.59 (*Ph*), 82.34 (*C*(CH_3)$_2$), 72.23 (O*C*HCH$_3$), 24.94 (OCH*C*H$_3$), 24.33 (C(*C*H$_3$)$_2$), 24.25 (C(*C*H$_3$)$_2$) ppm.

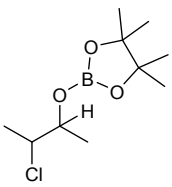
2-(1-(2-nitrophenyl)ethoxy)-pinacolborane (3h): ^{1}H NMR (CDCl$_3$, 200 MHz, 298 K): δ7.79 (d, $^3J_{H\text{-}H}$=8.21 Hz,2H, Ar*H*), 7.51 (t, 1H, Ar*H*), 7.27 (t, 1H, Ar*H*), 5.73(q,

1H, BpinOC*H*), 1.50 (d, $^{3}J_{H\text{-}H}$= 6.32 Hz, 3H, OCHCH_3), 1.12 (s, 6H, C(CH_3)$_2$), 1.08 (s, 6H, C(CH_3)$_2$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 147.11 (Ar*C*-NO_2), 140.23 (Ar*C*-R), 133.26 (*Ph*), 127.62 (*Ph*), 127.46 (*Ph*), 123.75 (*Ph*), 82.77 (*C*(CH$_3$)$_2$), 68.02 (O*C*HCH$_3$), 24.51 (OCH*C*H$_3$), 24.42 (C(*C*H$_3$)$_2$), 24.46 (C(*C*H$_3$)$_2$) ppm.

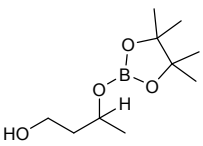
2-(benzhydryloxy)-pinacolborane (3i): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.33-7.29 (m, 4H, Ar*H*), 7.22-7.10 (m, 6H, Ar*H*), 6.13 (s, 1H, BpinOC*H*), 1.09 (s, 12H, C(CH_3)$_2$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 142.96 (Ar*C*-R), 128.13 (*Ph*), 128.02 (*Ph*), 127.09 (*Ph*), 126.30 (*Ph*), 82.69 (*C*(CH$_3$)$_2$), 77.76 (O*C*HPh), 24.27 (C(*C*H$_3$)$_2$) ppm; ^{11}B NMR (C_6D_6, 128 MHz, 298 K): δ 22.86 ppm.



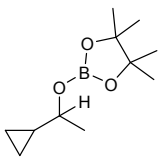
2-((3-chlorobutan-2-yl)oxy)-pinacolborane (3j): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 4.19 (q, 1H, OC*H*CH$_3$), 3.86 (q, 1H, -C*H*ClCH$_3$), 1.37 (dd, 3H, CHClCH_3), 1.22-1.18 (dd, 3H, OCHCH_3), 1.17 (s, 12H, C(CH_3)$_2$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 82.56 (*C*(CH$_3$)$_2$), 73.72 (d, O*C*HCHClCH$_3$), 60.44 (d, OCH*C*HClCH$_3$), 24.26 (C(*C*H$_3$)$_2$), 24.18 (C(*C*H$_3$)$_2$), 19.63 (d, O(CHClCH$_3$)CH*C*H$_3$), 18.29 (d, CHCl*C*H$_3$) ppm.



2-((3-methylbutan-2-yl)oxy)-pinacolborane (3k): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 3.87 (q, 1H, OC*H*CH$_3$), 1.66-1.47 (m, 1H, C*H*(CH$_3$)), 1.16 (s, 12H, C(CH_3)$_2$), 1.06 (d, $^{3}J_{H\text{-}H}$= 6.32 Hz, 3H, OCHCH_3), 0.82 (d, $^{3}J_{H\text{-}H}$= 3.03 Hz, 3H, CH(CH_3)), 0.79 (d, $^{3}J_{H\text{-}H}$= 3.03 Hz, 3H, CH(CH_3)) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 82.13 (*C*(CH$_3$)$_2$), 75.21 (O*C*HCH$_3$), 34.13 (OCH*C*(CH$_3$)$_2$), 24.34 (C(*C*H$_3$)$_2$), 24.28 (C(*C*H$_3$)$_2$), 19.16 (OCH*C*H$_3$), 17.98 (CH(*C*H$_3$)$_2$), 17.56 (CH(*C*H$_3$)$_2$) ppm.



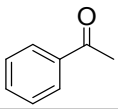
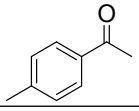
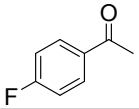
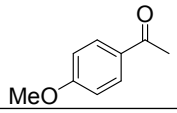
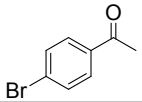
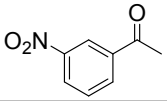
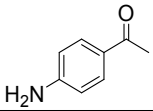
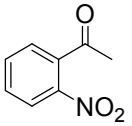
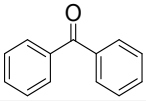
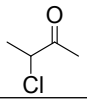
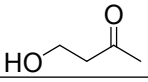
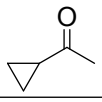
3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)butan-1-ol (3l): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 4.25 (s, 1H, OH), 4.05-3.98 (m, 1H, OC*H*CH$_3$), 3.91-3.72 (m, 3H, CH_2OH), 1.75-1.52 (m, 2H, CH_2CH$_2$OH), 1.15 (s, 12H, C(CH_3)$_2$), 1.15 (d, $^{3}J_{H\text{-}H}$= 7.33 Hz, 3H, OCHCH_3) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 82.38 (*C*(CH$_3$)$_2$), 68.30 (*C*H$_2$OH), 61.61 (O*C*HCH$_3$), 39.49 (*C*H$_2$CH$_2$OH), 24.54 (OCH*C*H$_3$), 24.30 (C(*C*H$_3$)$_2$) ppm.



2-(1-cyclopropylethoxy)-pinacolborane (3m): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 3.48 (q, 1H, OC*H*CH$_3$), 1.20 (d, $^{3}J_{H\text{-}H}$= 6.32 Hz, 3H, OCHCH_3), 1.15 (s, 12H, C(CH_3)$_2$), 0.92-0.77 (m, 2H, CyCH_2), 0.37-0.30 (m, 2H, CyCH_2), 0.12-0.04

(m, 1H, CyC*H*) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 82.19 ($C(CH_3)_2$), 74.72 ($OCHCH_3$), 24.38 ($C(CH_3)_2$), 24.22 ($C(CH_3)_2$), 22.11 ($OCHCH_3$), 18.12 (Cy*C*H), 2.74 (CyCH_2), 1.96 (CyCH_2) ppm.

Table S4. TOF(h^{-1}) table for ketone hydroboration

Entry	Substrate	NMR Yield(%)	TOF(h^{-1})
3a		94[a]/95[b]/98[c]	313[a]/237[b]/490[c]
3b		99[a]/94[b]/>99[c]	330[a]/235[b]/>495[c]
3c		99[a]/99[b]/97[c]	330[a]/247[b]/485[c]
3d		>99[a]/>99[b]/>99[c]	>330[a]/>247[b]/>495[c]
3e		98[a]/99[b]/99[c]	326[a]/247[b]/495[c]
3f		>99[a]/93[b]/>99[c]	>330[a]/232[b]/>495[c]
3g		98[a]/>99[b]/99[c]	326[a]/>247[b]/495[c]
3h		98[a]/95[b]/97[c]	326[a]/237[b]/485[c]
3i		99[a]/>99[b]/>99[c]	330[a]/>247[b]/>495[c]
3j		99[a]/>99[b]/95[c]	330[a]/>247[b]/475[c]
3k		99[a]/78[b]/95[c]	330[a]/195[b]/475[c]
3l		86[a]/65[b]/84[c]	286[a]/162[b]/420[c]
3m		94[a]/98[b]/98[c]	313[a]/245[b]/490[c]

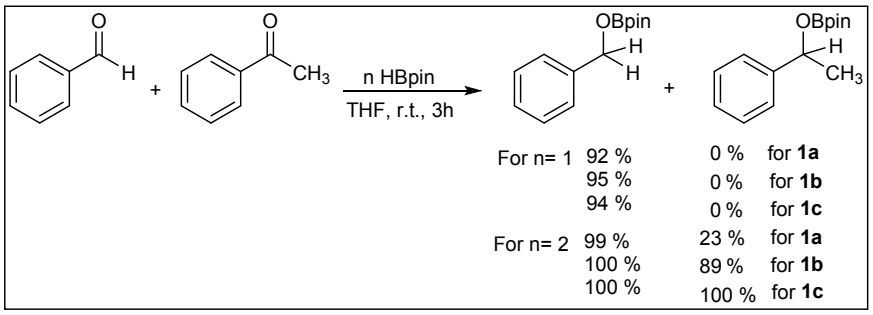
Reaction conditions: Catalyst: 0.1 mol% , Reaction conditions: room temperature in THF. Reaction time: **1a**: 3 h, **1b**: 2 h, **1c**: 2 h. Yields are calculated w.r.t. mesitylene as internal standard. Superscripts a, b and c stand for the catalyst **1a**, **1b** and **1c**. TOF(h^{-1}) are calculated per active site in catalysts.

Competitive experiment for aldehyde/ketone hydroboration-selectivity study:

Three different reaction with 1 equiv. benzaldehyde (0.5 mmol), 1 equiv. acetophenone (0.5 mmol),1 equiv. pinacolborane (0.5 mmol), 0.5 mL stock solution of **1a**, **1b** and **1c** catalyst (0.1 mol%) in THF were charged in a Schlenk tube with a magnetic bead inside the glove box. The reaction mixture was allowed to stir at room temperature for 3 h.

Another three reaction with 1 equiv. benzaldehyde (0.5 mmol), 1 equiv. acetophenone (0.5 mmol),2 equiv. pinacolborane (0.5 mmol), 0.5 mL stock solution of **1a**, **1b** and **1c** catalyst (0.1 mol%) in THF were charged in a Schlenk tube with a magnetic bead inside the glove box. The reaction mixture was allowed to stir at room temperature for 3 h.

Upon completion of reaction, the solvent was removed using high vacuum in Schlenk line and mesitylene (0.5 mmol) as internal standard, was added while making the NMR in $CDCl_3$.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.



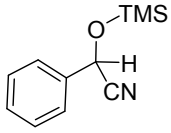
Scheme S1. Competitive aldehyde/ketone hydroboration selectivity study. Reaction conditions: 0.1mol% catalyst. Yields were determined by ^1H NMR integration relative to mesitylene.

General catalytic procedure for the cyanosilylation of aldehydes and ketones:

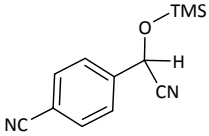
Aldehyde or ketones (0.5 mmol), TMSCN (0.5 mmol), 0.5 mL stock solution of catalyst (0.1 mol%) in THF were charged in a Schlenk tube with a magnetic bead inside the glove box. The reaction mixture was allowed to stir at room temperature for 1h for aldehydes and 2 h for ketones for**1a**, **1b** and **1c**, respectivly. Upon completion of reaction, the solvent was removed

using high vacuum in Schlenk line and mesitylene (0.5 mmol) as internal standard, was added while making the NMR in $CDCl_3$.The progress of the reaction was monitored by ^1H and ^{13}C NMR spectroscopy.

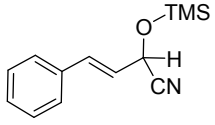
Analytical data and NMR (^1H, ^{13}C) spectra of cyanosilylated products of corresponding aldehydes and ketones:

2-phenyl-2-((trimethylsilyl)oxy)acetonitrile (4a): ^1H NMR ($CDCl_3$, 200 MHz, 298 K): δ 

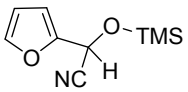
7.25-7.20 (m, 5H, Ar*H*), 5.37 (s, 1H, C*H*OSi$(CH_3)_3$), 0.14 (s, 9H, Si(CH_3)$_3$) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 136.25 (Ar*C*-R), 129.17 (*Ph*), 128.78 (*Ph*), 126.23 (*Ph*), 119.04 (*C*N), 63.52 (*C*HOSi$(CH_3)_3$), -0.44 (Si(*C*H_3)$_3$) ppm.

4-(cyano((trimethylsilyl)oxy)methyl)benzonitrile (4b): ^1H NMR ($CDCl_3$, 200 MHz, 298 

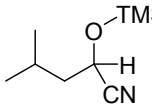
K): δ 7.60-7.46 (m, 5H, Ar*H*), 5.45 (s, 1H, C*H*OSi$(CH_3)_3$), 0.19 (s, 9H, Si(CH_3)$_3$) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 140.93 (*Ph*), 132.41 (*Ph*), 126.59 (*Ph*), 118.07 (Ar-*C*N), 117.85, 122.94 (CN), 62.50 (*C*HOSi$(CH_3)_3$), -0.68 (Si(*C*H_3)$_3$) ppm.

(E)-4-phenyl-2-((trimethylsilyl)oxy)but-3-enenitrile (4c): ^1H NMR ($CDCl_3$, 200 MHz, 298 

K): δ 7.29-7.17 (m, 5H, Ar*H*), 6.70 (d, $^3J_{H\text{-}H}$= 16.2 Hz, 1H, PhC*H*CH), 6.06 (dd, 1H, $^3J_{H,H}$= 16.08 Hz, PhCHC*H*), 4.96 (d, $^3J_{H,H}$= 5.93 Hz, 1H, C*H*OSi$(CH_3)_3$), 0.16 (s, 9H, CHCHOSi(CH_3)$_3$) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 134.93 (Ar*C*-R), 133.76 (*Ph*), 128.61 (ArCH=*C*HCH(OTMS)(CN)), 123.47 (Ar*C*H=CHCH(OTMS)(CN)), 118.26 (*C*N), 62.07 (*C*HOSi$(CH_3)_3$), -0.30 (Si(*C*H_3)$_3$) ppm.

2-(furan-2-yl)-2-((trimethylsilyl)oxy)acetonitrile (4d): ^1H NMR ($CDCl_3$, 200 MHz, 298 K): 

δ 7.32 (s, 1H, Ar*H*), 6.42 (d,$^3J_{H\text{-}H}$ = 3.28 Hz, 1H, Ar*H*), 6.27 (dd,$^3J_{H\text{-}H}$ = 3.59 Hz, 1H, Ar*H*), 5.40 (s, 1H, C*H*OSi$(CH_3)_3$), 0.10 (s, 9H, Si(CH_3)$_3$ ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 148.25 (*Ar*), 143.66 (*Ar*), 116.99 (*C*N), 110.64 (*Ar*), 109.51 (*Ar*), 57.27 (*C*HOSi$(CH_3)_3$), -0.62 (Si(*C*H_3)$_3$) ppm.

4-methyl-2-((trimethylsilyl)oxy)pentanenitrile (4e): ^1H NMR ($CDCl_3$, 200 MHz, 298 K): δ 

4.33 (t, 1H, C*H*OSi$(CH_3)_3$), 1.82-1.52 (m, 2H, $CH_2CH(CH_3)_2$), 1.82-1.52 (m, 1H, $CH_2CH(CH_3)_2$), 0.87 (d, $^3J_{H\text{-}H}$ = 4.67 Hz, 3H, CH(CH_3)$_2$), 0.84 (d, $^3J_{H\text{-}H}$ = 6.44 Hz, 3H, CH(CH_3)$_2$), 0.13 (s, 9H, Si(CH_3)$_3$) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 120.02 (CN), 59.69 (*C*HOSi$(CH_3)_3$), 44.79 ($CH_2CH(CH_3)_2$), 23.59 ($CH_2CH(CH_3)_2$), 22.33 ($CH_2CH(CH_3)_2$), 21.69 ($CH_2CH(CH_3)_2$), -0.64 (Si(*C*H_3)$_3$) ppm.

2-phenyl-2-((trimethylsilyl)oxy)propanenitrile (4f): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.46 (dd, $^{3}J_{H\text{-}H}$= 8.31 Hz, 2H, Ar*H*), 7.32-7.21 (m, 3H, Ar*H*), 1.75 (s, 3H, CCH_3OTMS), 0.10 (s, 9H,Si(CH_3)$_3$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 141.90 (Ar*C*-R), 128.47 (*Ph*), 124.44 (*Ph*), 121.40 (*C*N), 71.46 (*C*HOSi(CH$_3$)$_3$), 33.36 (CH*C*H$_3$), 0.85 (Si(*C*H$_3$)$_3$) ppm.

2-(p-tolyl)-2-((trimethylsilyl)oxy)propanenitrile (4g): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.36-7.32 (d, $^{3}J_{H\text{-}H}$= 8.21 Hz, 2H, Ar*H*), 7.10-7.06 (d, $^{3}J_{H\text{-}H}$= 8.34 Hz, 2H, Ar*H*), 2.25 (s, 3H, Ar-CH_3), 1.74 (s, 3H, CCH_3OTMS), 0.08 (s, 9H, Si(CH_3)$_3$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 139.01 (*Ph*), 138.34 (*Ph*), 129.14 (*Ph*), 124.46 (*Ph*), 121.59 (*C*N), 71.39 (*C*HOSi(CH$_3$)$_3$), 33.38 (CH*C*H$_3$), 20.88 (Ar-*C*H$_3$), 0.91 (Si(*C*H$_3$)$_3$) ppm.

2-(4-bromophenyl)-2-((trimethylsilyl)oxy)propanenitrile (4h): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.43-7.29 (m, 4H, Ar*H*), 1.72 (s, 3H, CCH_3OTMS), 0.11 (s, 9H, Si(CH_3)$_3$) ppm.

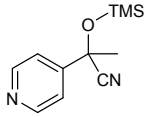
2-(4-aminophenyl)-2-((trimethylsilyl)oxy)propanenitrile (4i): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 8.35-8.33 (m, 1H, Ar*H*), 8.13-8.09 (d, $^{3}J_{H\text{-}H}$ = 8.08 Hz, 1H, Ar*H*), 7.83-7.79 (d, $^{3}J_{H\text{-}H}$=7.83Hz, 1H, Ar*H*), 7.49 (t, 1H, Ar*H*), 1.81 (s, 3H, CCH_3OTMS), 0.19 (s, 9H, Si(CH_3)$_3$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 148.25 (Ar*C*-NO$_2$), 148.28 (Ar*C*-R), 130.39 (*Ph*), 129.69 (*Ph*), 123.40 (*Ph*), 120.49 (*Ph*), 119.55 (*C*N), 70.53 (*C*HOSi(CH$_3$)$_3$), 32.99 (CH*C*H$_3$), 0.78 (Si(*C*H$_3$)$_3$) ppm.

2-(4-methoxyphenyl)-2-((trimethylsilyl)oxy)propanenitrile (4j): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.39-7.35 (d, $^{3}J_{H\text{-}H}$= 8.72 Hz, 2H, Ar*H*), 6.82-6.78 (d, $^{3}J_{H\text{-}H}$ =8.72Hz, 2H, Ar*H*), 3.68 (s, 3H, OCH_3), 1.74 (s, 3H, CCH_3OTMS), 0.08 (s, 9H, Si(CH_3)$_3$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 159.65 (Ar*C*-OMe), 133.83 (*Ph*), 125.85 (*Ph*), 121.57 (*Ph*), 113.69 (*C*N), 71.70 (*C*HOSi(CH$_3$)$_3$), 54.96 (OCH_3), 33.20 (CH*C*H$_3$), 0.86 (Si(*C*H$_3$)$_3$) ppm.

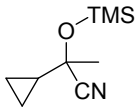
2,2-diphenyl-2-((trimethylsilyl)oxy)acetonitrile (4k): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.46-7.41 (m, 4H, Ar*H*), 7.27-7.16 (m, 6H, Ar*H*), 0.08 (s, 9H, Si(CH_3)$_3$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 141.88 (Ar*C*-R), 128.50

(*Ph*), 128.40 (*Ph*), 125.74 (*Ph*), 120.53 (*C*N), 76.24 (*C*HOSi(CH_3)$_3$), 0.76 (Si(*C*H_3)$_3$) ppm.

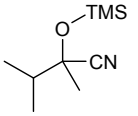
2-(pyridin-4-yl)-2-((trimethylsilyl)oxy)propanenitrile (4l): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 8.59-8.56 (d, $^3J_{H\text{-}H}$= 5.94 Hz, 2H, Ar*H*), 7.37-7.34 (d, $^3J_{H\text{-}H}$=6.06 Hz, 2H, Ar*H*), 1.73 (s, 3H, CC*H*$_3$OTMS), 0.15 (s, 9H,Si(C*H*$_3$)$_3$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 150.67(*Ar*), 150.60 (*Ar*), 150.12 (*Ar*), 120.91 (*Ar*), 120.22 (*Ar*), 119.03 (*C*N), 70.30 (*C*HOSi(CH_3)$_3$), 32.75 (CH*C*H$_3$), 0.73 (Si(*C*H$_3$)$_3$) ppm.



2-cyclopropyl-2-((trimethylsilyl)oxy)propanenitrile (4m): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.53(s, 3H, CC*H*$_3$OTMS), 1.06 (q, 1H, C*H*C(CH$_3$)(CN)OTMS), 0.56-0.39 (m, 4H, C*H*$_2$), 0.15 (s, 9H,Si(C*H*$_3$)$_3$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 120.79 (*C*N), 70.39 (*C*HOSi(CH_3)$_3$), 29.34 (C*C*H$_3$OTMS), 21.45 (*C*HC(CH$_3$)(CN)OTMS), 2.35(*C*H$_2$), 1.79 (*C*H$_2$), 1.12 (Si(*C*H$_3$)$_3$) ppm.



2,3-dimethyl-2-((trimethylsilyl)oxy)butanenitrile (4n): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 1.75 (sept, 1H, C*H*C(CH$_3$)(CN)OTMS), 1.41 (s, 3H, CC*H*$_3$OTMS), 0.96-0.92 (m, 6H, C(C*H*$_3$)$_2$), 0.16 (s, 9H, Si(C*H*$_3$)$_3$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28 MHz, 298 K): δ 121.35 (*C*N), 73.31 (*C*HOSi(CH_3)$_3$), 38.97 (OCH*C*(CH$_3$)$_2$), 25.83 (C*C*H$_3$OTMS), 16.99 (CH(*C*H$_3$)$_2$), 16.76 (CH(*C*H$_3$)$_2$), 1.01 (Si(*C*H$_3$)$_3$) ppm.



3-chloro-2-methyl-2-((trimethylsilyl)oxy)butanenitrile (4o): ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 3.94 (quat, 1H, C*H*C(CH$_3$)(CN)OTMS), 1.54 (s, 3H, CC*H*$_3$OTMS), 1.47-1.44 (d, $^3J_{H\text{-}H}$ = 6.69 Hz, 3H, CH(C*H*$_3$)Cl), 0.19 (s, 9H, Si(C*H*$_3$)$_3$) ppm.

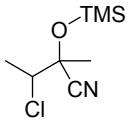
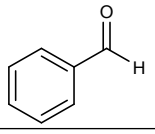
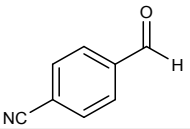
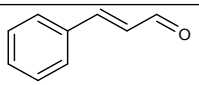
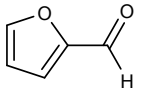
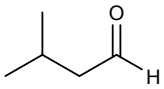
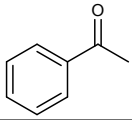
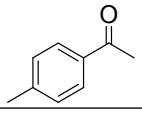
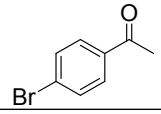
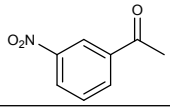
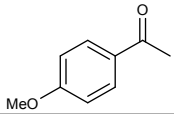
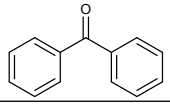
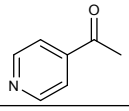
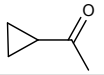
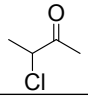
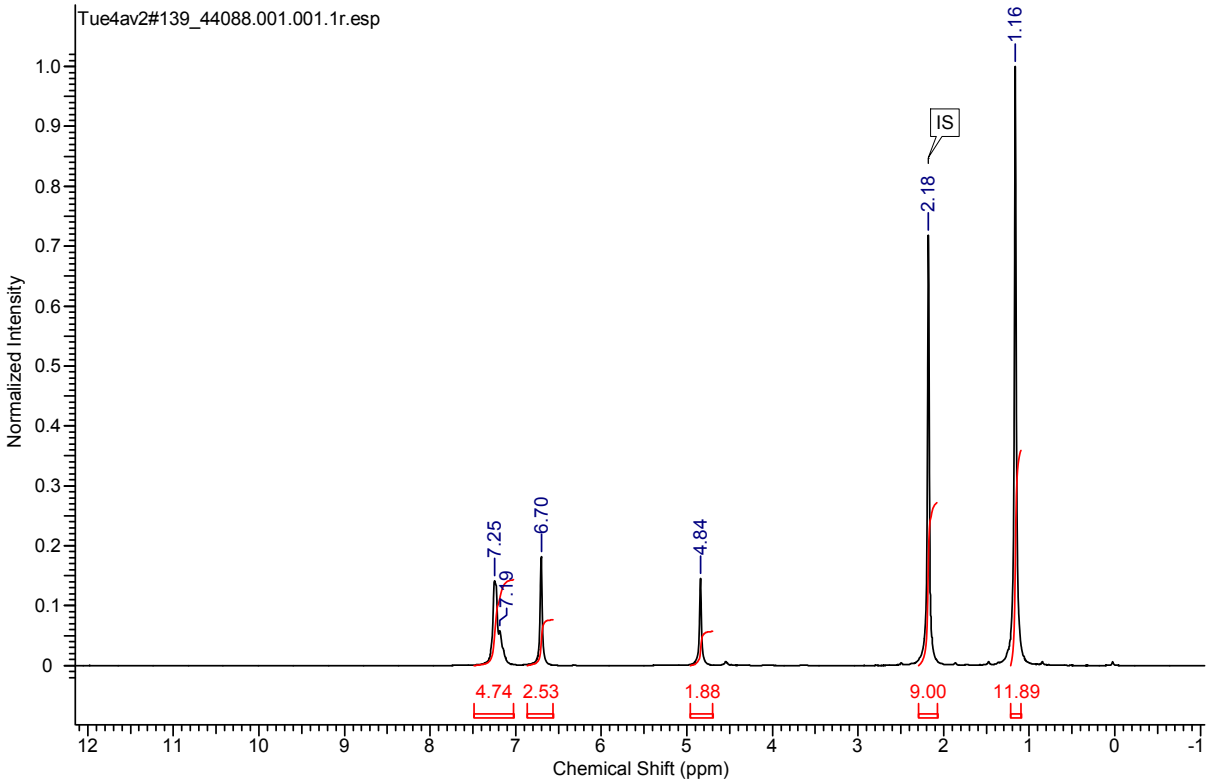


Table S5: TON and TOF(h^{-1}) table for aldehydes and ketone cyanosilyaltion by 1a,1b and 1c.

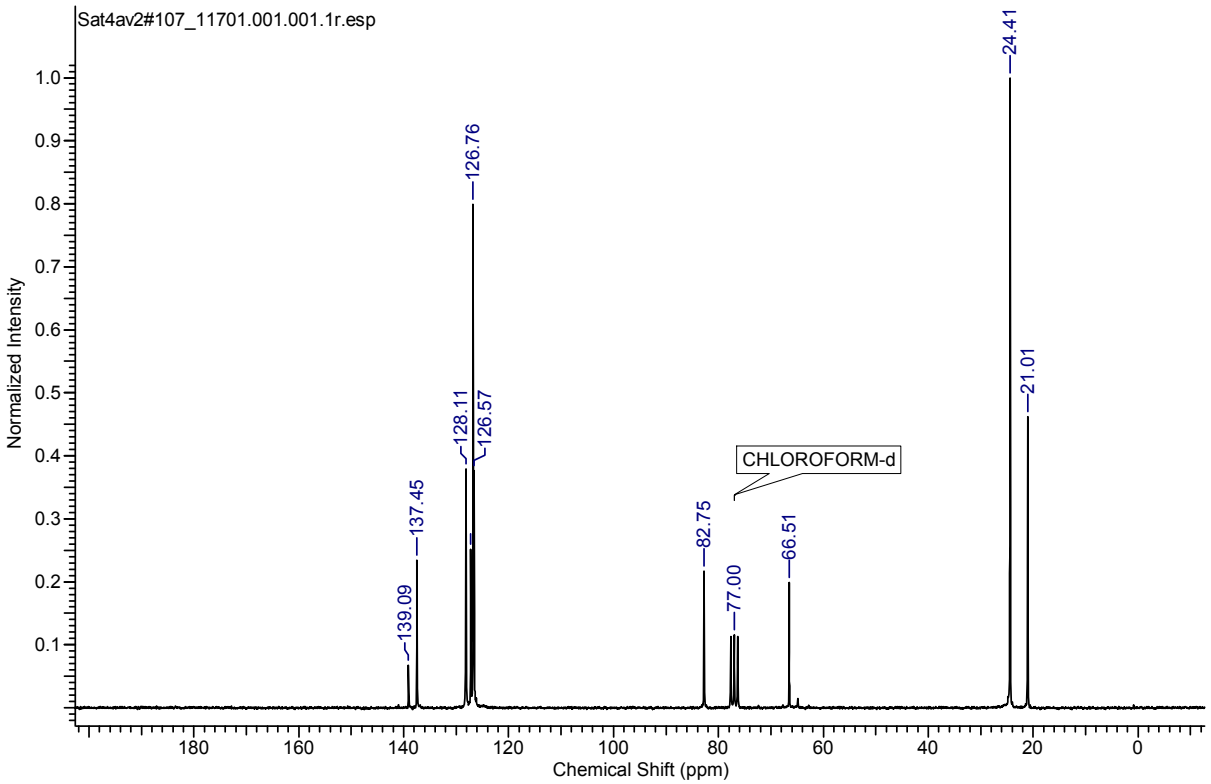
Entry	Substrate	Catalyst (mol%)	Time (h)	NMR Yield (%)	TON	TOF (h^{-1})
4a.		0.1	1	87[a]/84[b]/86[c]	870[a]/840[b]/860[c]	870[a]/840[b]/860[c]
4b.		0.1	1	83[a]/87[b]/86[c]	830[a]/870[b]/860[c]	415[a]/435[b]/860[c]
4c.		0.1	1	91[a]/92[b]/90[c]	910[a]/920[b]/900[c]	910[a]/920[b]/900[c]
4d.		0.1	1	83[a]/88[b]/80[c]	830[a]/880[b]/800[c]	830[a]/880[b]/800[c]
4e.		0.1	1	92[a]/87[b]/87[c]	920[a]/870[b]/870[c]	920[a]/870[b]/870[c]
4f.		0.1	2	93[a]/96[b]/98[c]	930[a]/960[b]/980[c]	465[a]/480[b]/490[c]
4g.		0.1	2	93[a]/95[b]/98[c]	930[a]/950[b]/980[c]	465[a]/475[b]/490[c]
4h.		0.1	2	98[a]/99[b]/99[c]	980[a]/990[b]/990[c]	490[a]/495[b]/495[c]
4i.		0.1	2	93[a]/87[b]/98[c]	930[a]/870[b]/980[c]	465[a]/435[b]/490[c]
4j.		0.1	2	99[a]/99[b]/99[c]	990[a]/990[b]/990[c]	495[a]/495[b]/495[c]
4k.		0.1	2	99[a]/99[b]/99[c]	990[a]/990[b]/990[c]	495[a]/495[b]/495[c]
4l.		0.1	2	89[a]/89[b]/85[c]	890[a]/890[b]/850[c]	445[a]/445[b]/425[c]
4m.		0.1	2	97[a]/90[b]/80[c]	970[a]/900[b]/800[c]	485[a]/450[b]/400[c]
4n.		0.1	2	90[a]/91[b]/80[c]	900[a]/910[b]/800[c]	450[a]/455[b]/400[c]
4o.		0.1	2	56[a]/51[b]/45[c]	560[a]/510[b]/450[c]	280[a]/255[b]/225[c]

Representative NMR spectra:

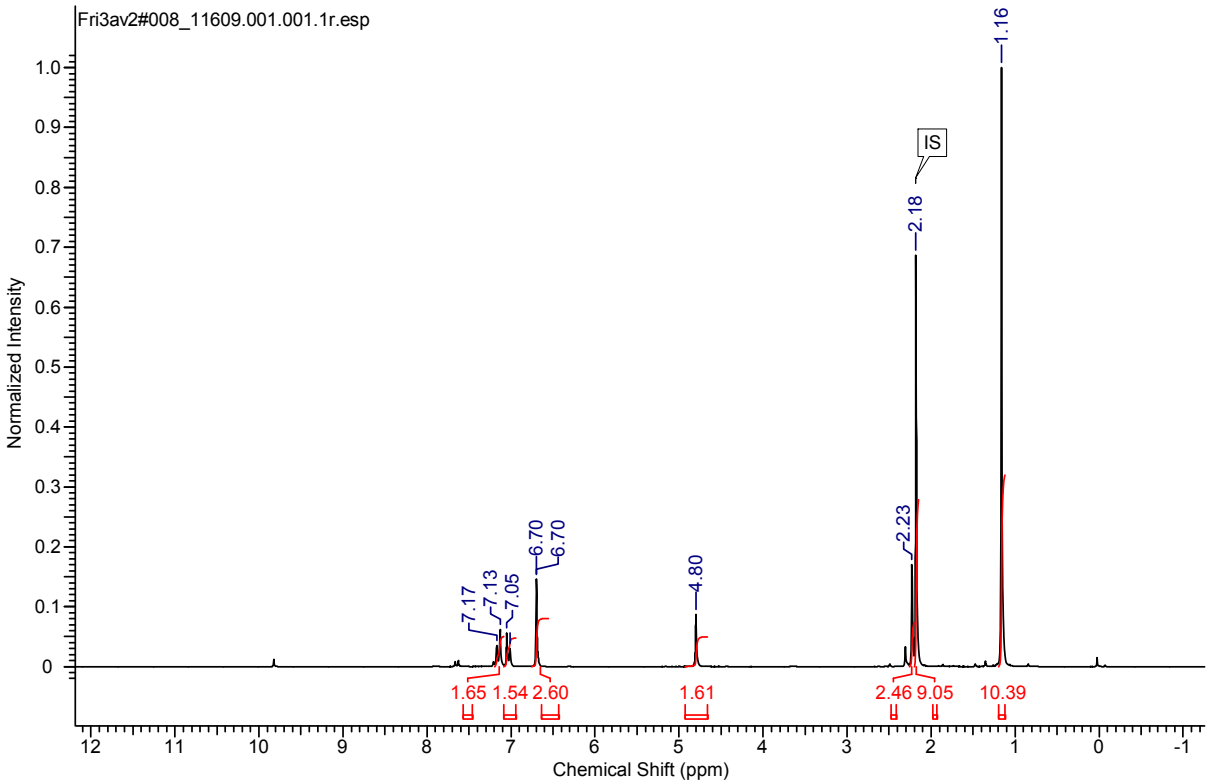
^{1}H NMR Spectrum of **2a** ($CDCl_3$, 200 MHz, 298 K)



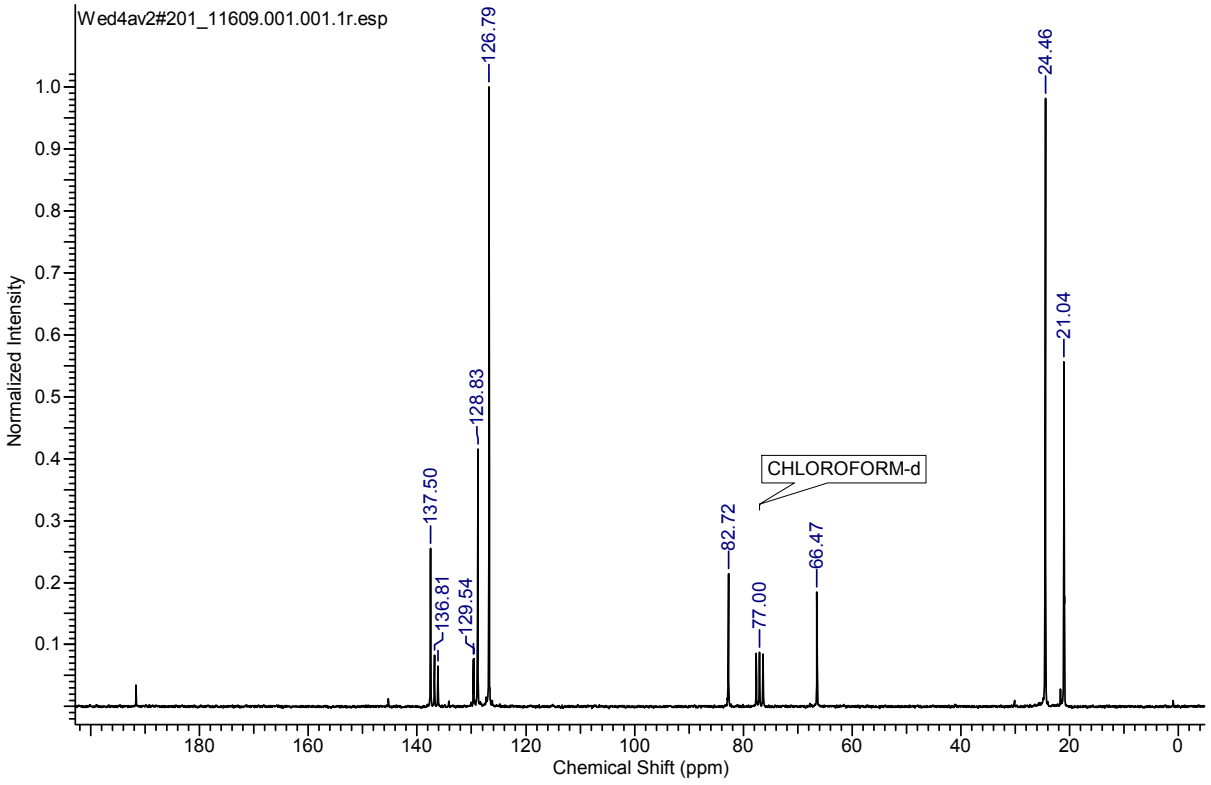
^{13}C NMR spectrum of **2a** ($CDCl_3$, 50.28 MHz, 298 K)



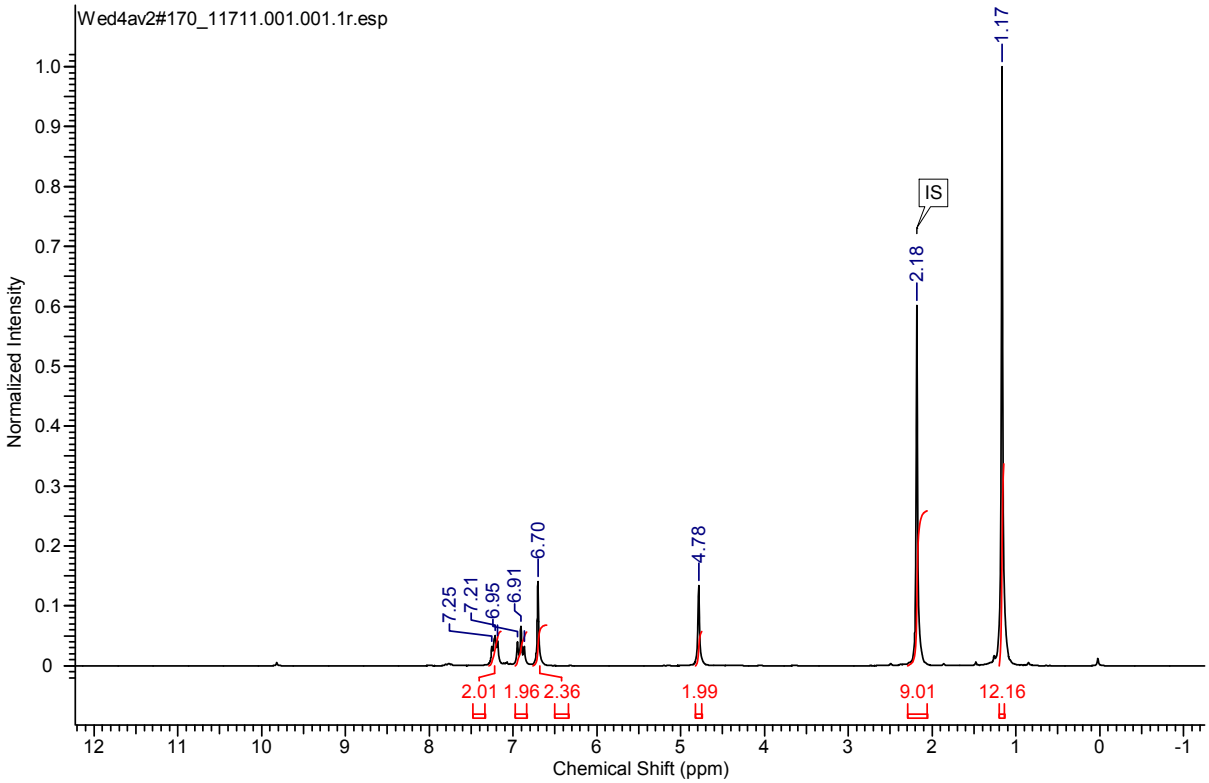
^{1}H NMR Spectrum of **2b** ($CDCl_3$, 200 MHz, 298 K)



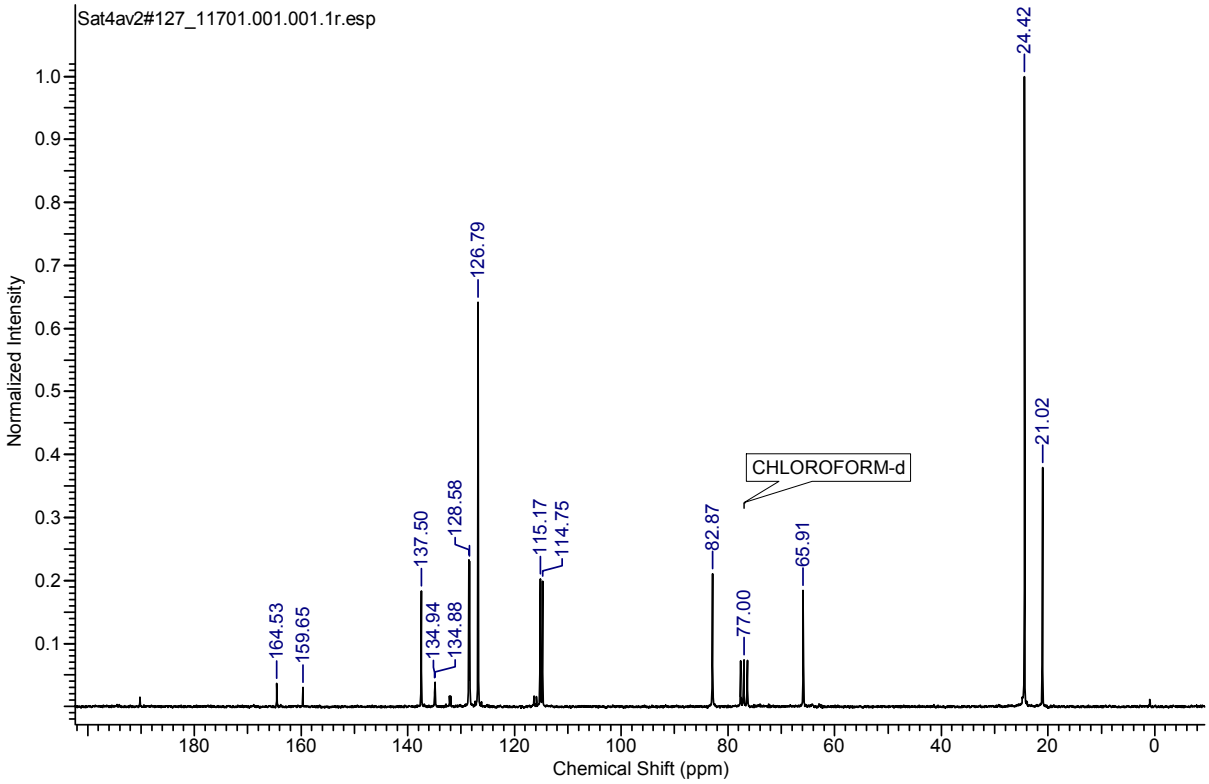
^{13}C NMR spectrum of **2b** ($CDCl_3$, 50.28 MHz, 298 K)



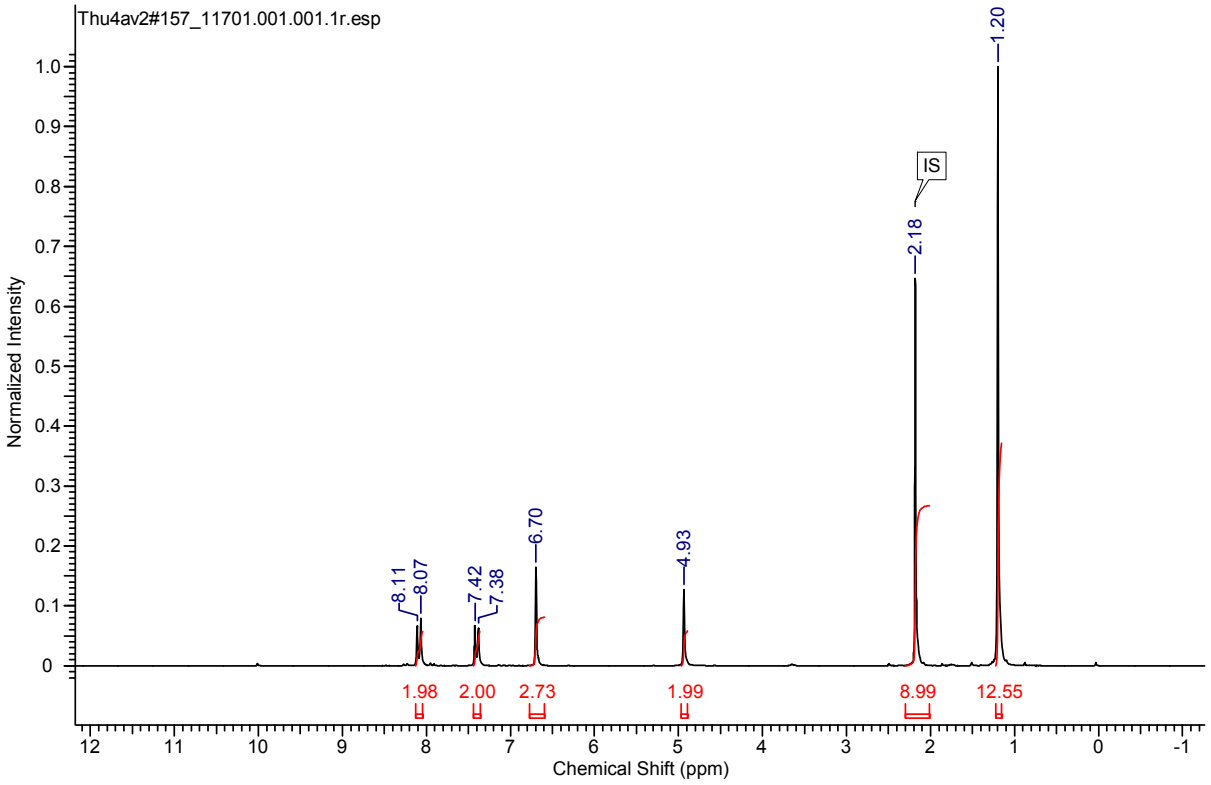
^{1}H NMR Spectrum of **2c** ($CDCl_3$, 200 MHz, 298 K)



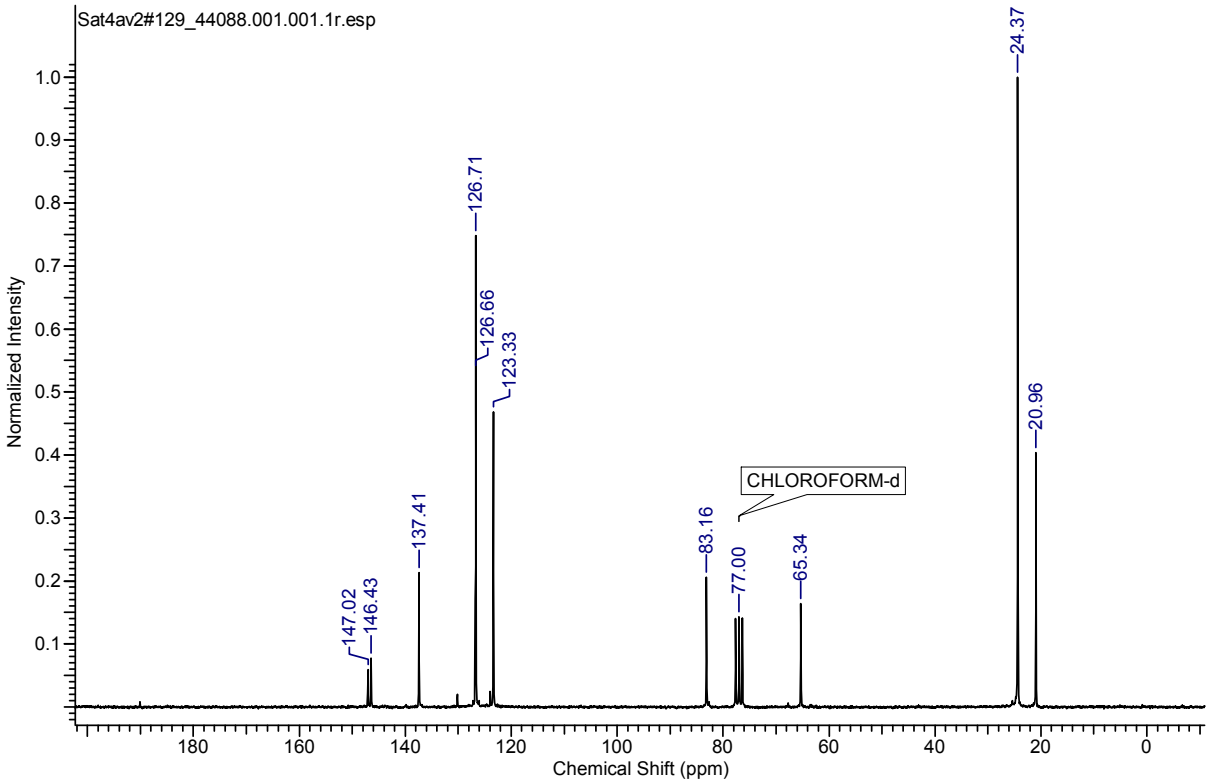
^{13}C NMR spectrum of **2c** ($CDCl_3$, 50.28 MHz, 298 K)



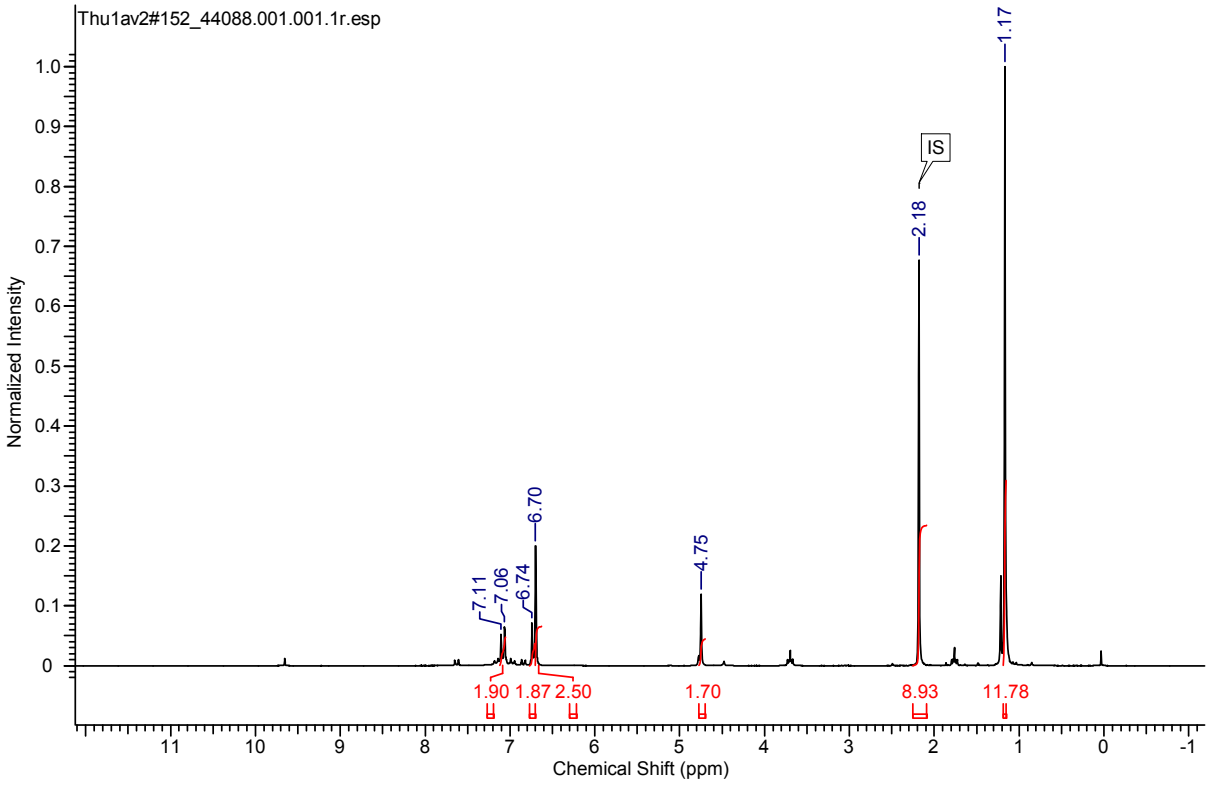
^{1}H NMR Spectrum of **2d** ($CDCl_3$, 200 MHz, 298 K)



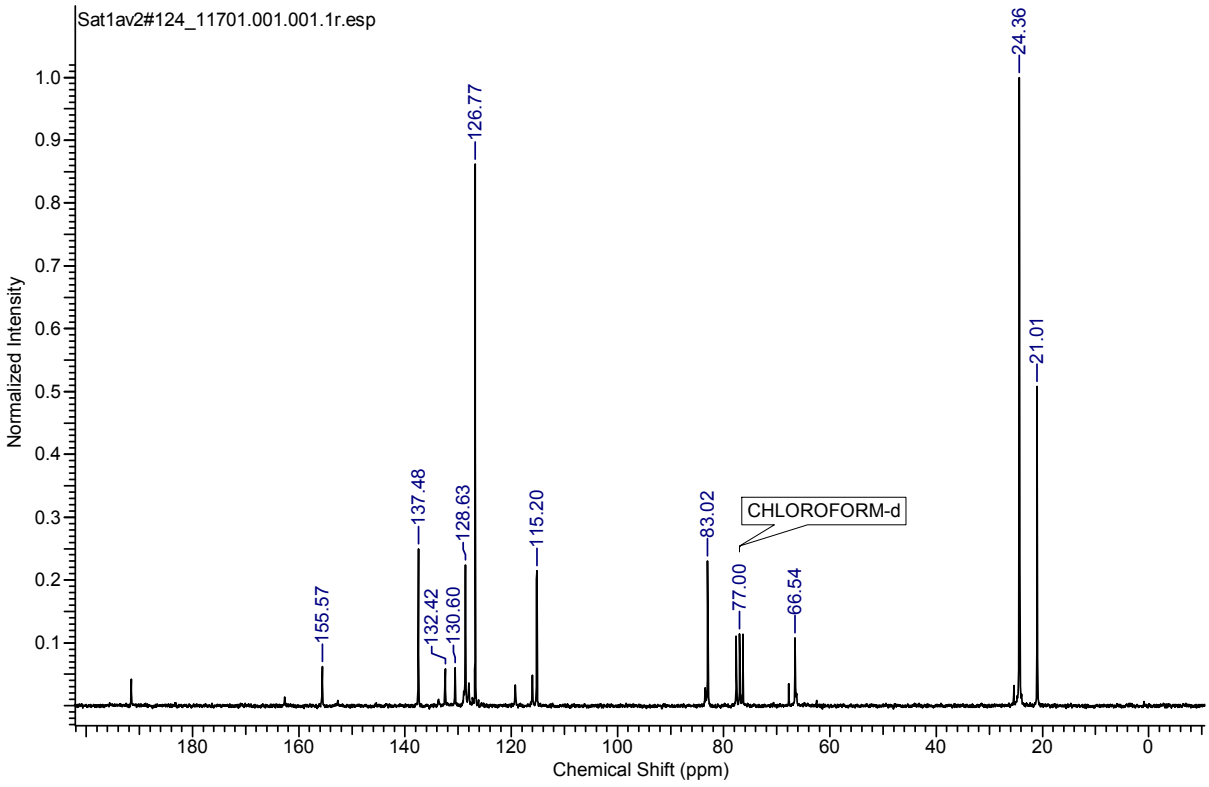
^{13}C NMR spectrum of **2d** ($CDCl_3$, 50.28 MHz, 298 K)



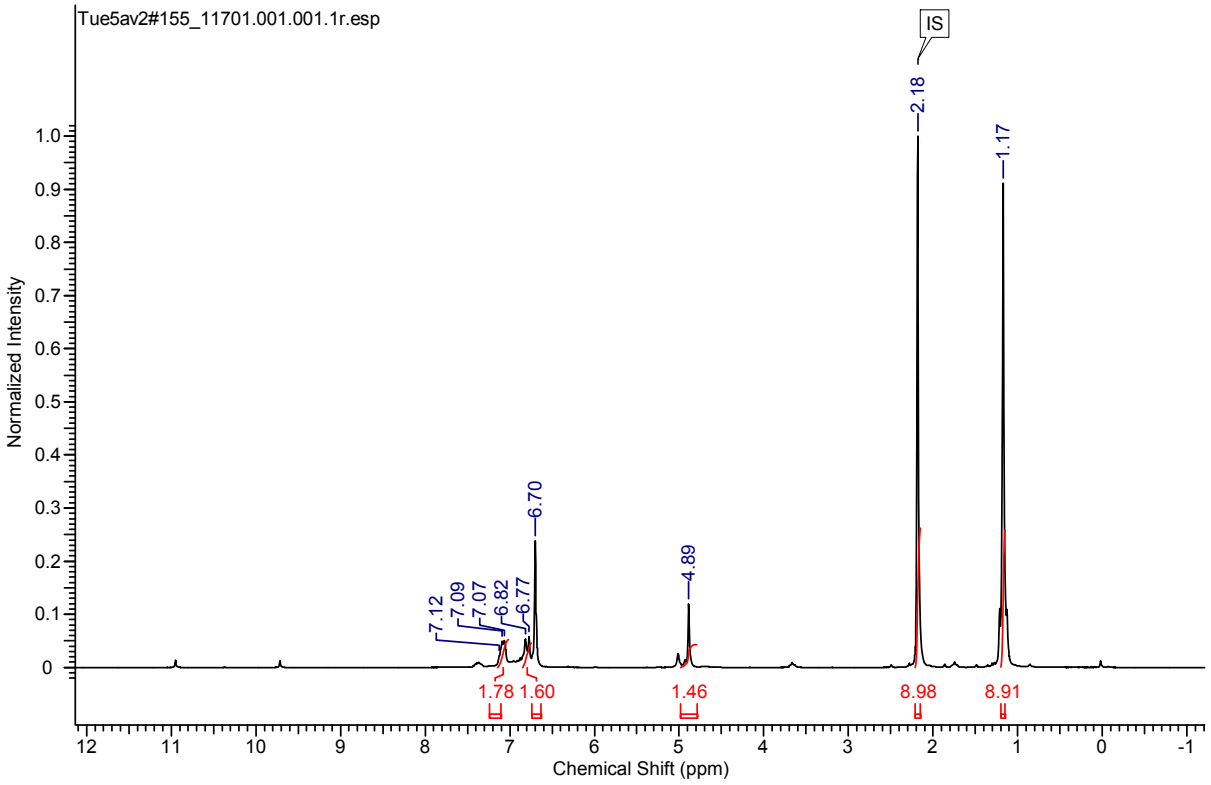
^{1}H NMR Spectrum of **2e** ($CDCl_3$, 200 MHz, 298 K)



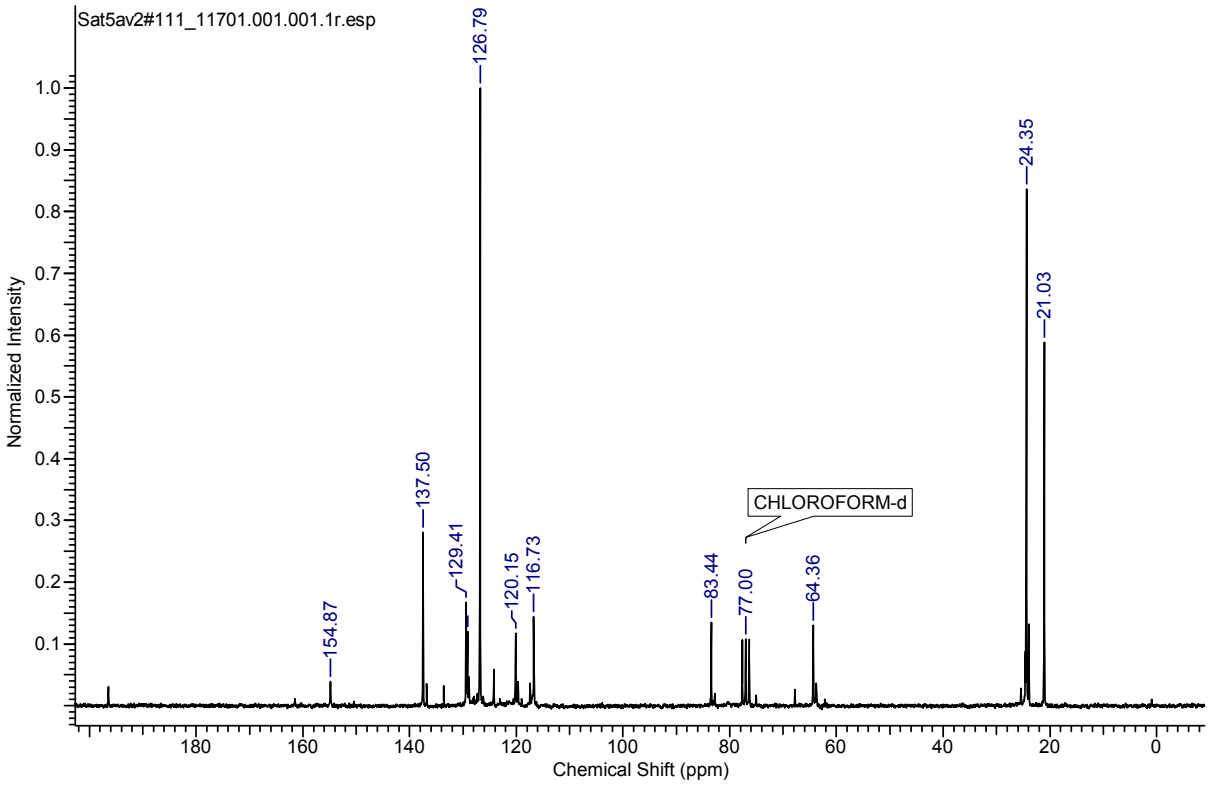
^{13}C NMR spectrum of **2e** ($CDCl_3$, 50.28 MHz, 298 K)



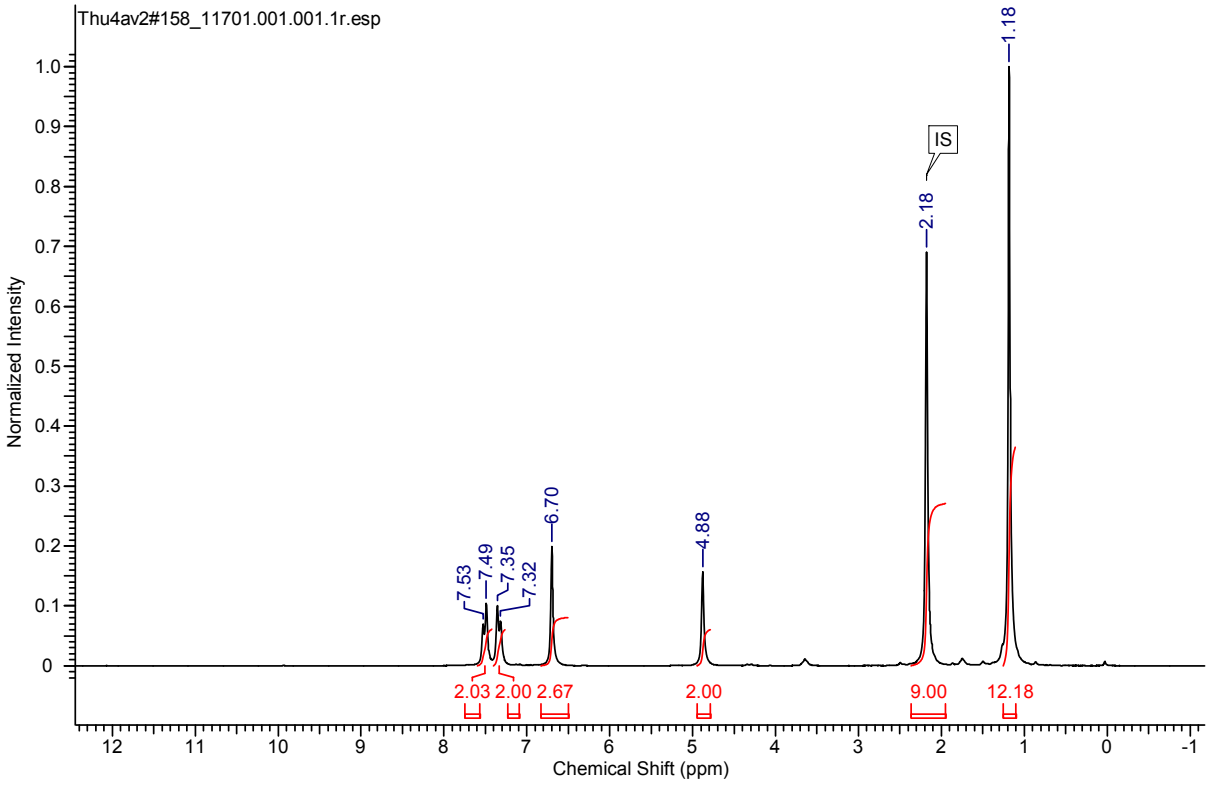
^{1}H NMR Spectrum of **2f** ($CDCl_3$, 200 MHz, 298 K)



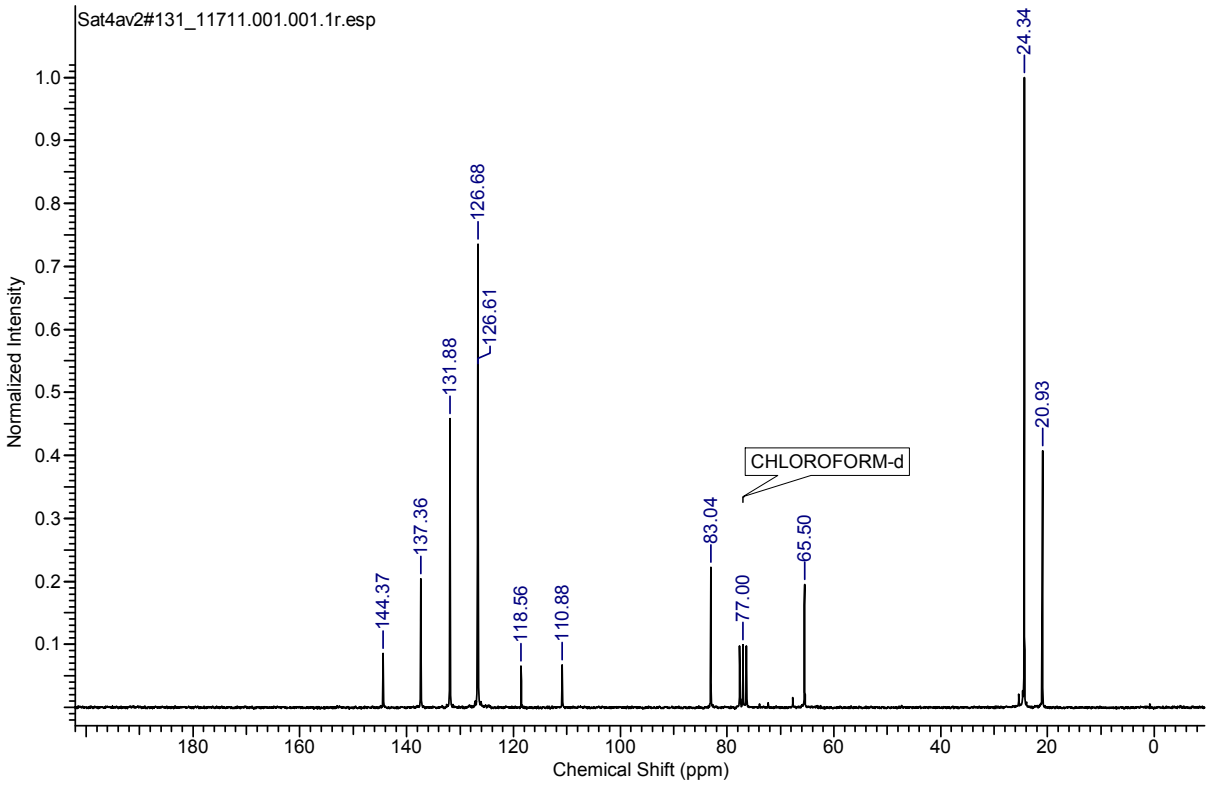
^{13}C NMR spectrum of **2f** ($CDCl_3$, 50.28 MHz, 298 K)



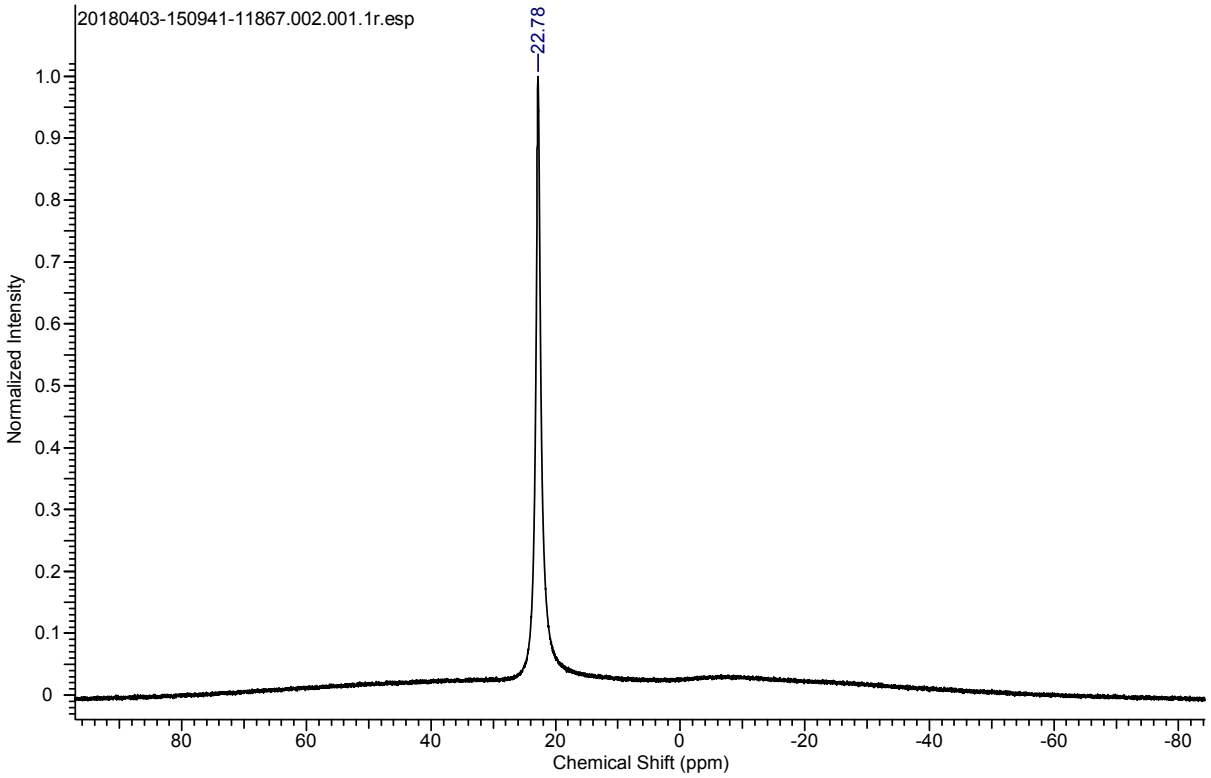
^{1}H NMR Spectrum of **2g** ($CDCl_3$, 200 MHz, 298 K)



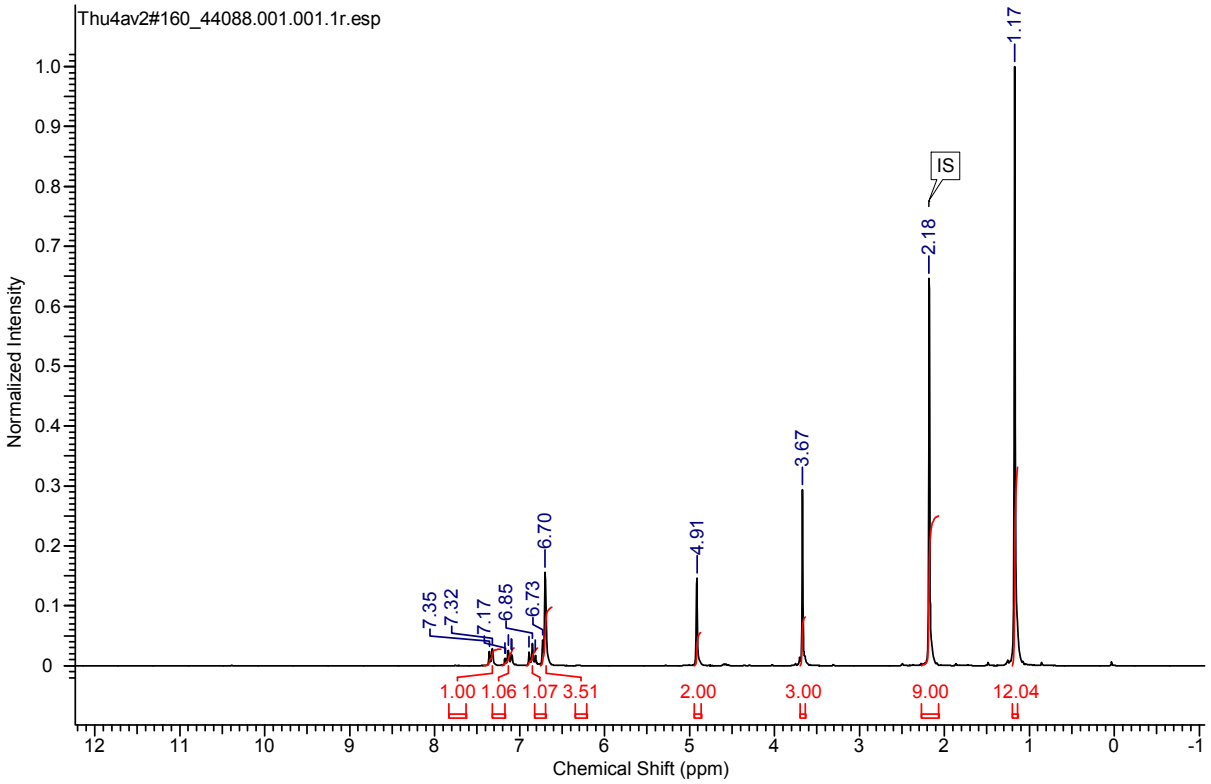
^{13}C NMR spectrum of **2g** ($CDCl_3$, 50.28 MHz, 298 K)



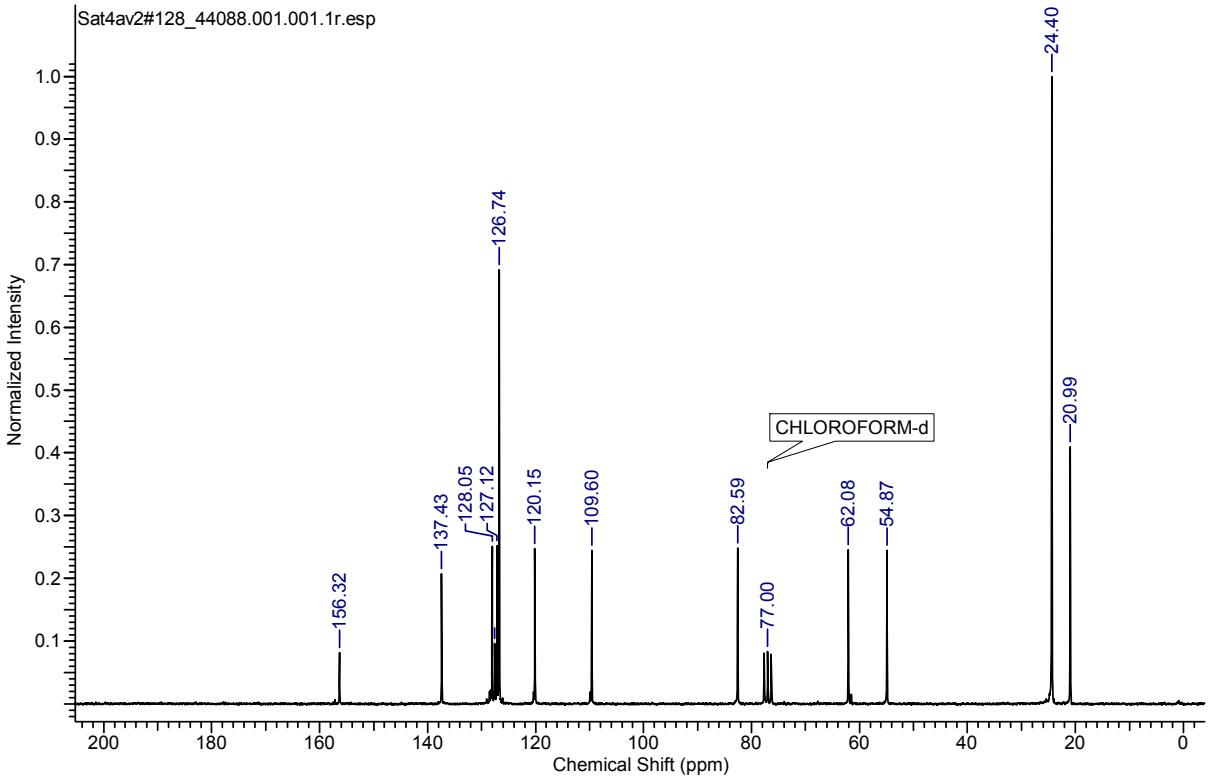
^{11}B NMR spectrum of **2g** (C_6D_6, 128 MHz, 298 K)



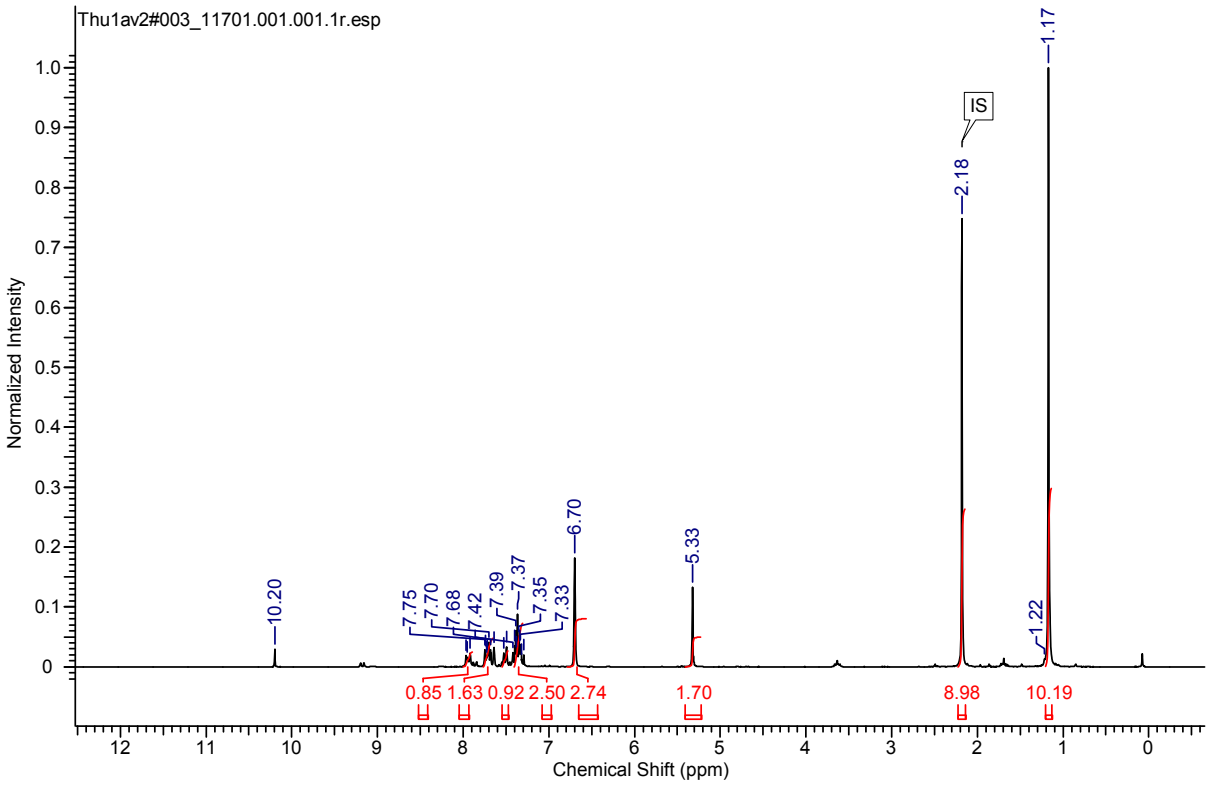
^{1}H NMR Spectrum of **2h** ($CDCl_3$, 200 MHz, 298 K)



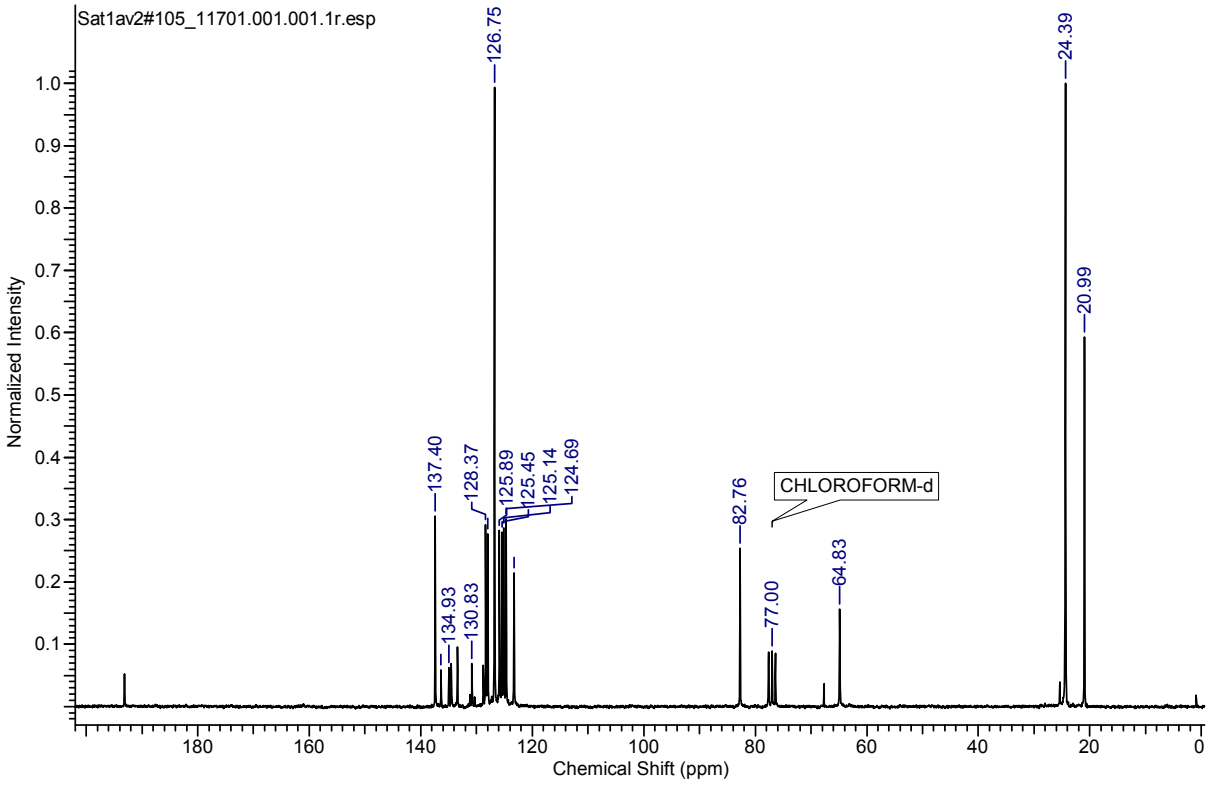
^{13}C NMR spectrum of **2h** ($CDCl_3$, 50.28 MHz, 298 K)



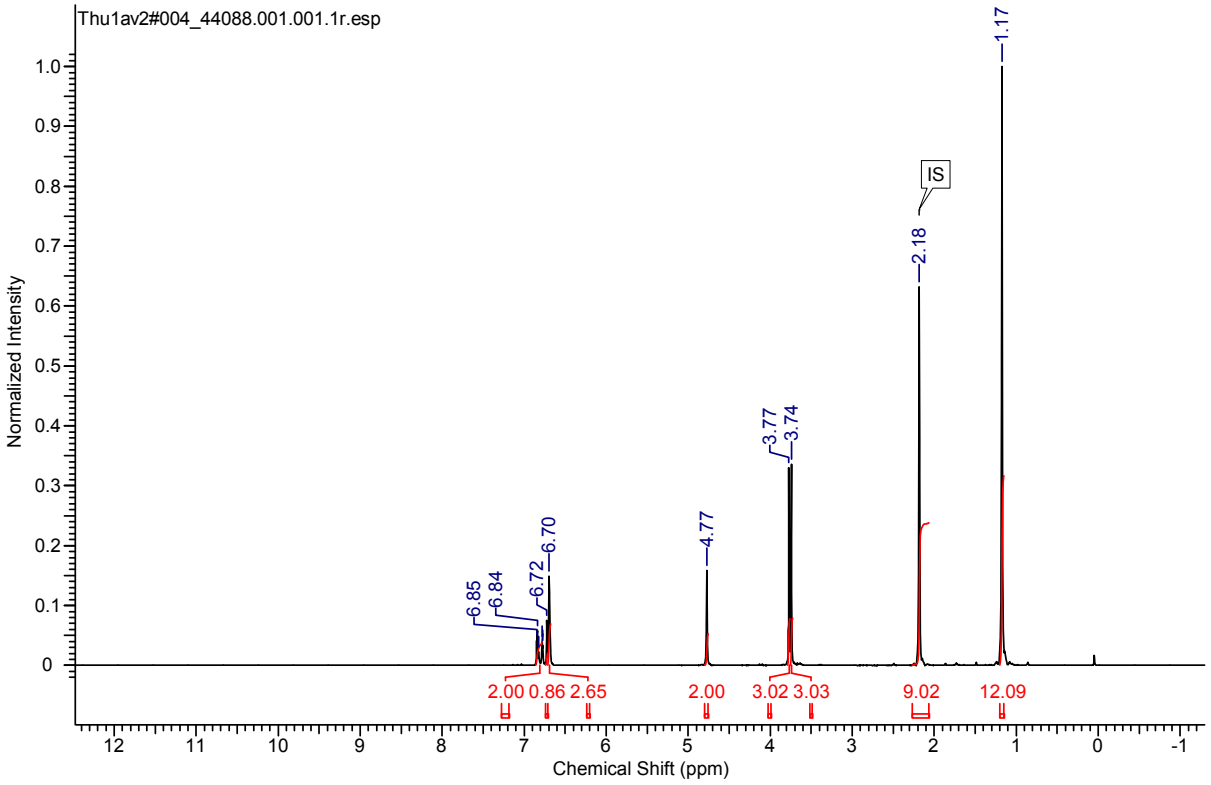
^{1}H NMR Spectrum of **2i** ($CDCl_3$, 200 MHz, 298 K)



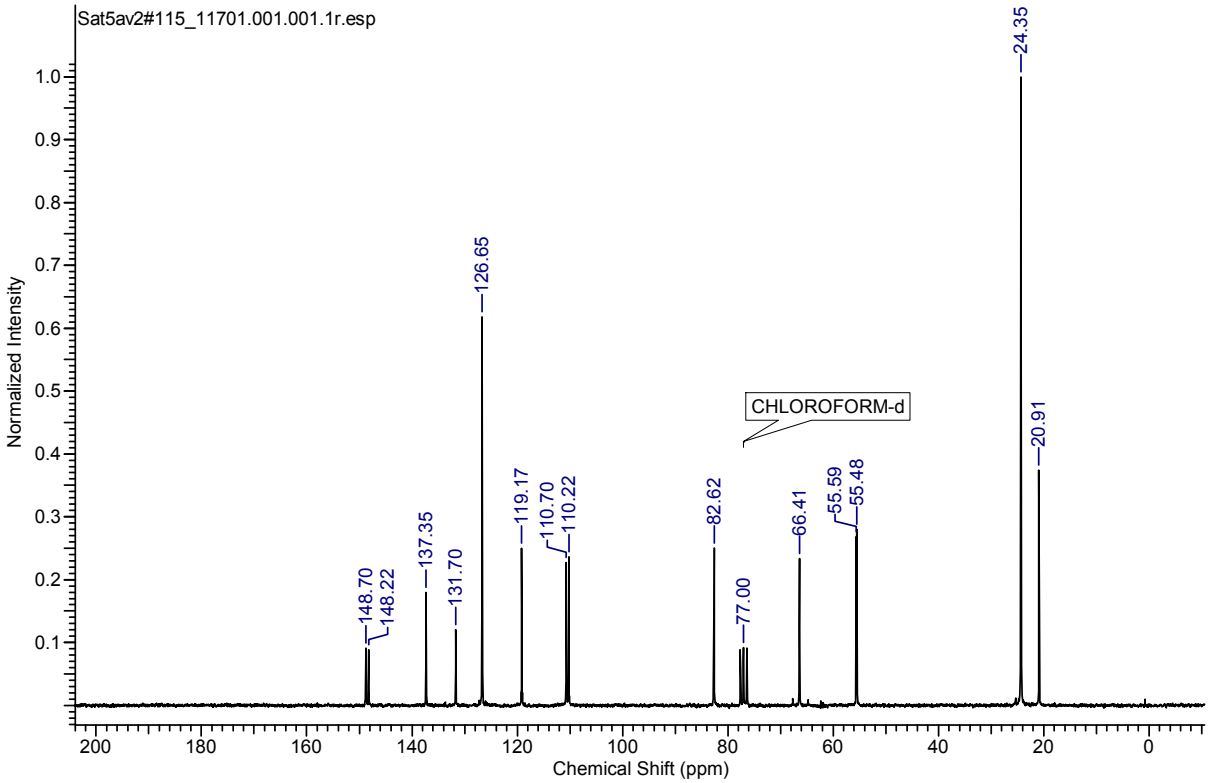
^{13}C NMR spectrum of **2i** ($CDCl_3$, 50.28 MHz, 298 K)



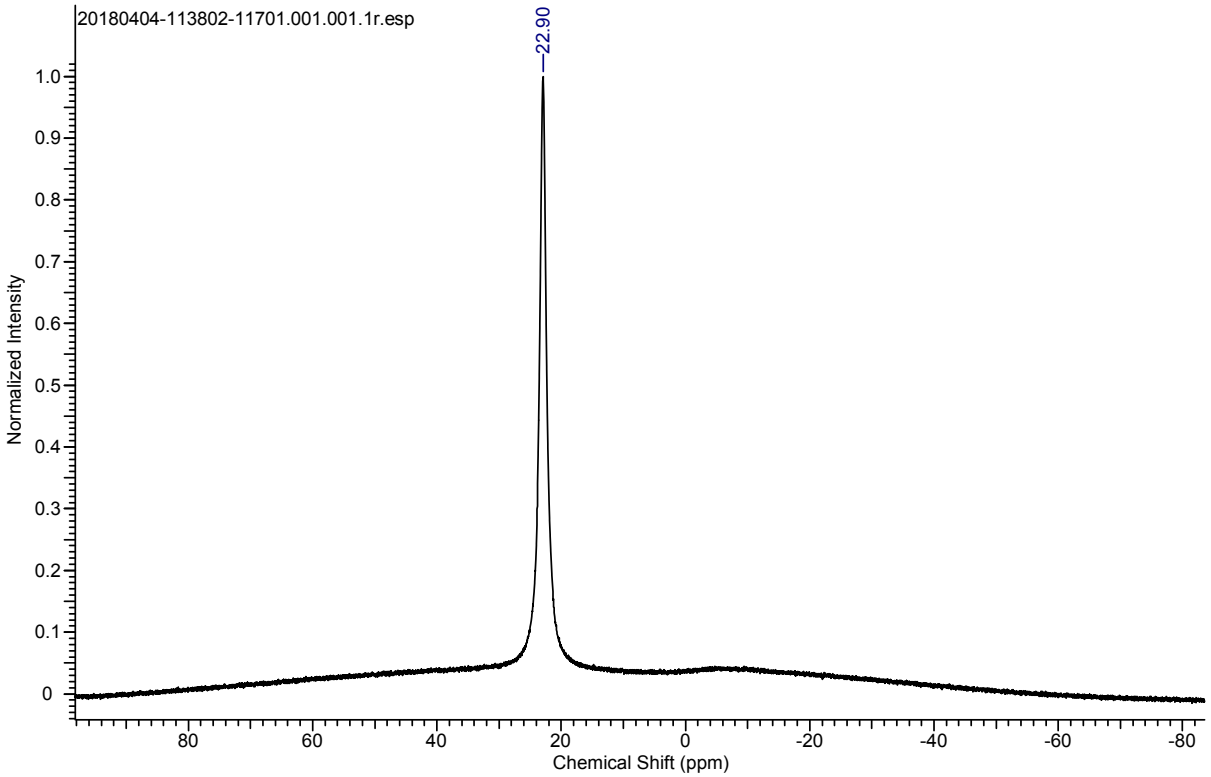
^{1}H NMR Spectrum of **2j** ($CDCl_3$, 200 MHz, 298 K)



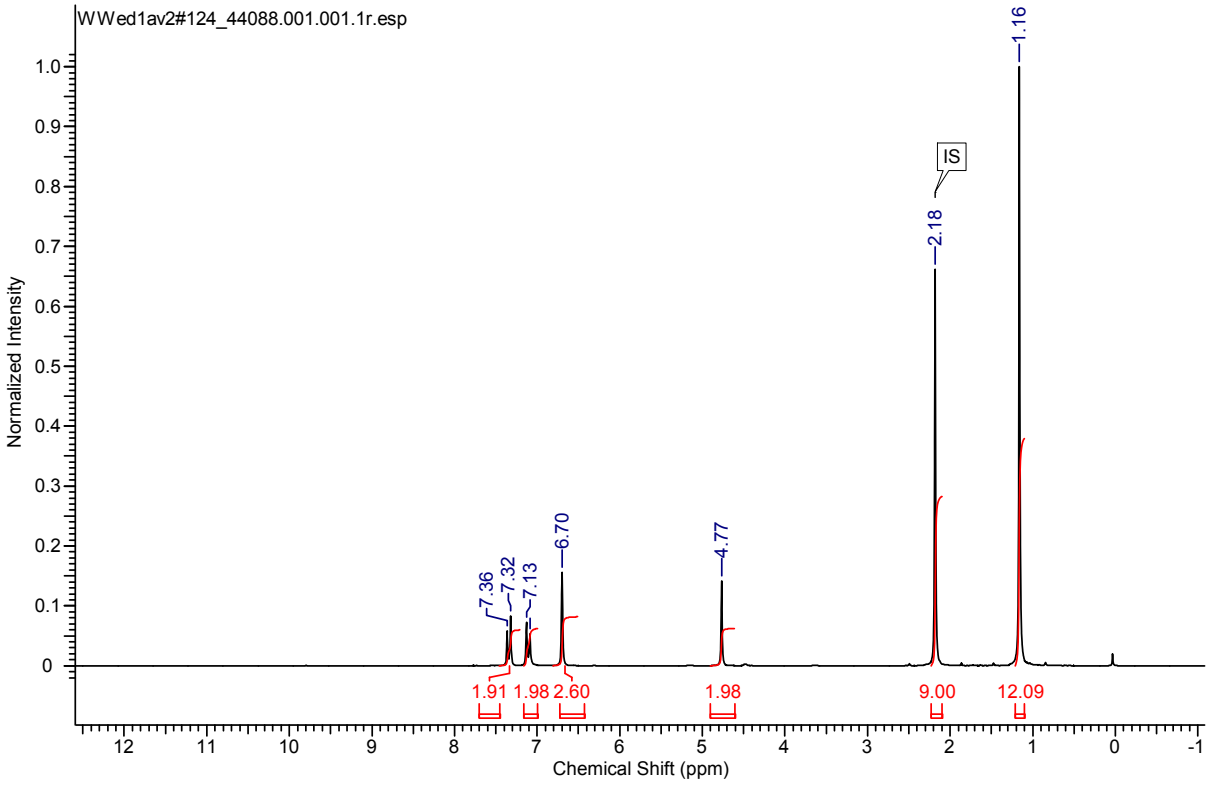
^{13}C NMR spectrum of **2j** ($CDCl_3$, 50.28 MHz, 298 K)



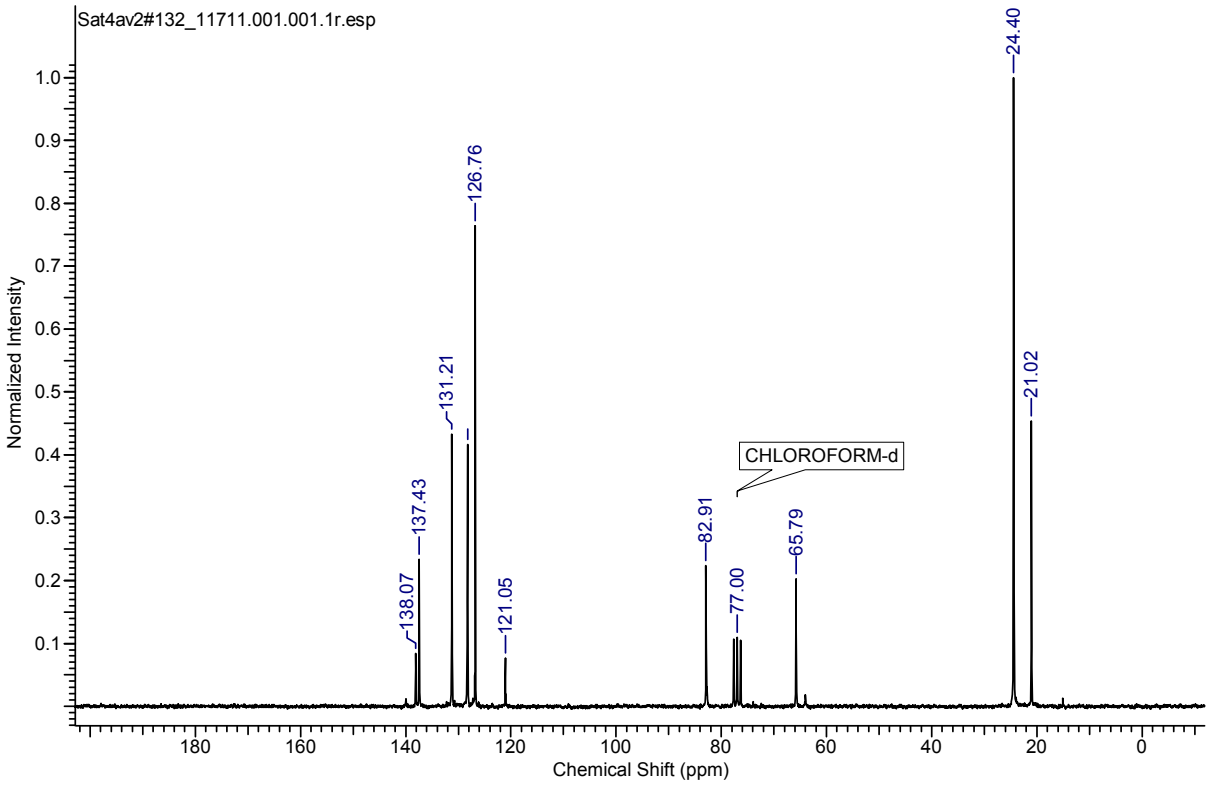
^{11}B NMR spectrum of **2j** (C_6D_6, 128 MHz, 298 K)



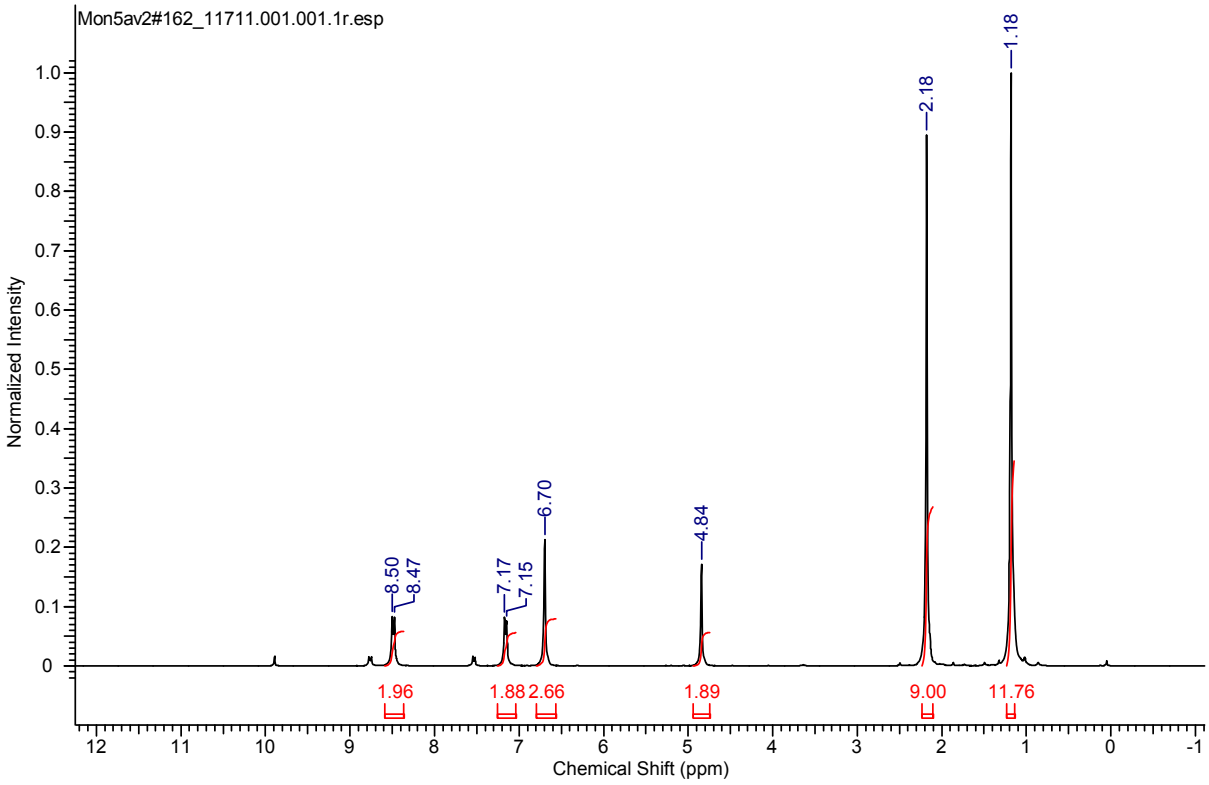
^{1}H NMR Spectrum of **2k** ($CDCl_3$, 200 MHz, 298 K)



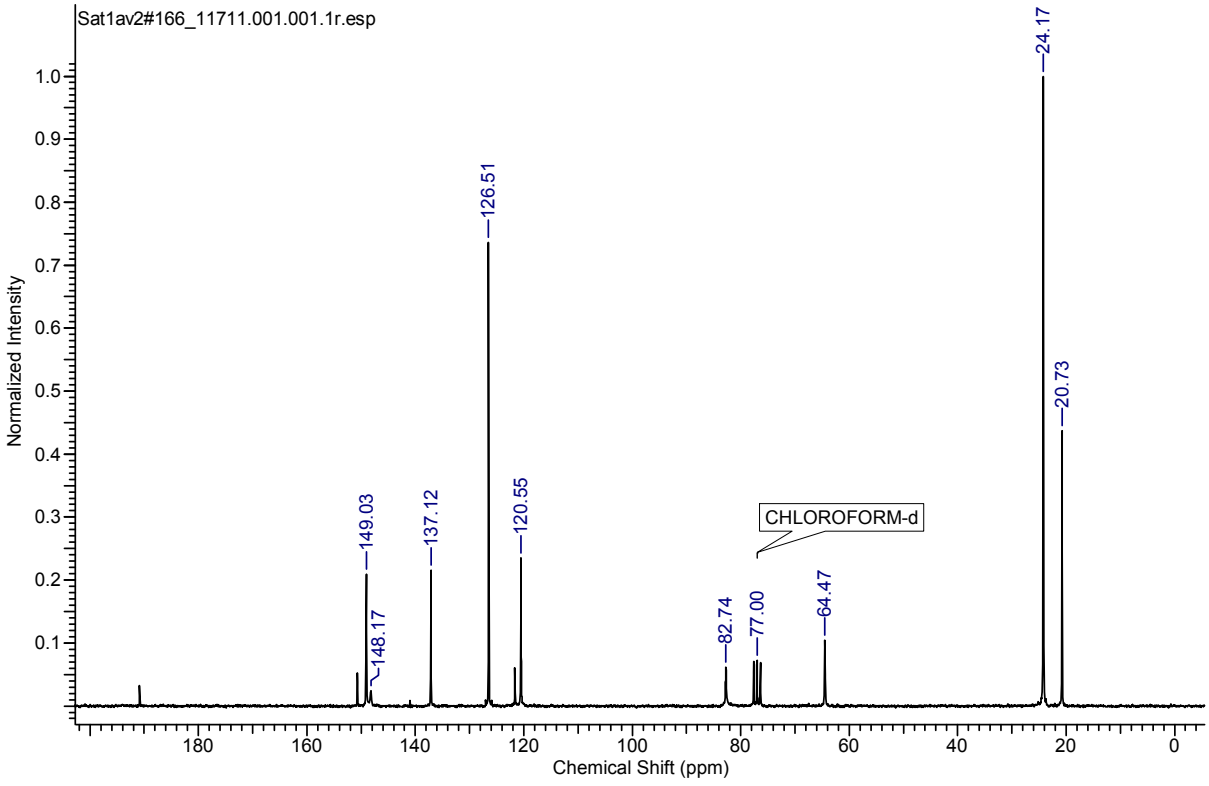
^{13}C NMR spectrum of **2k** ($CDCl_3$, 50.28 MHz, 298 K)



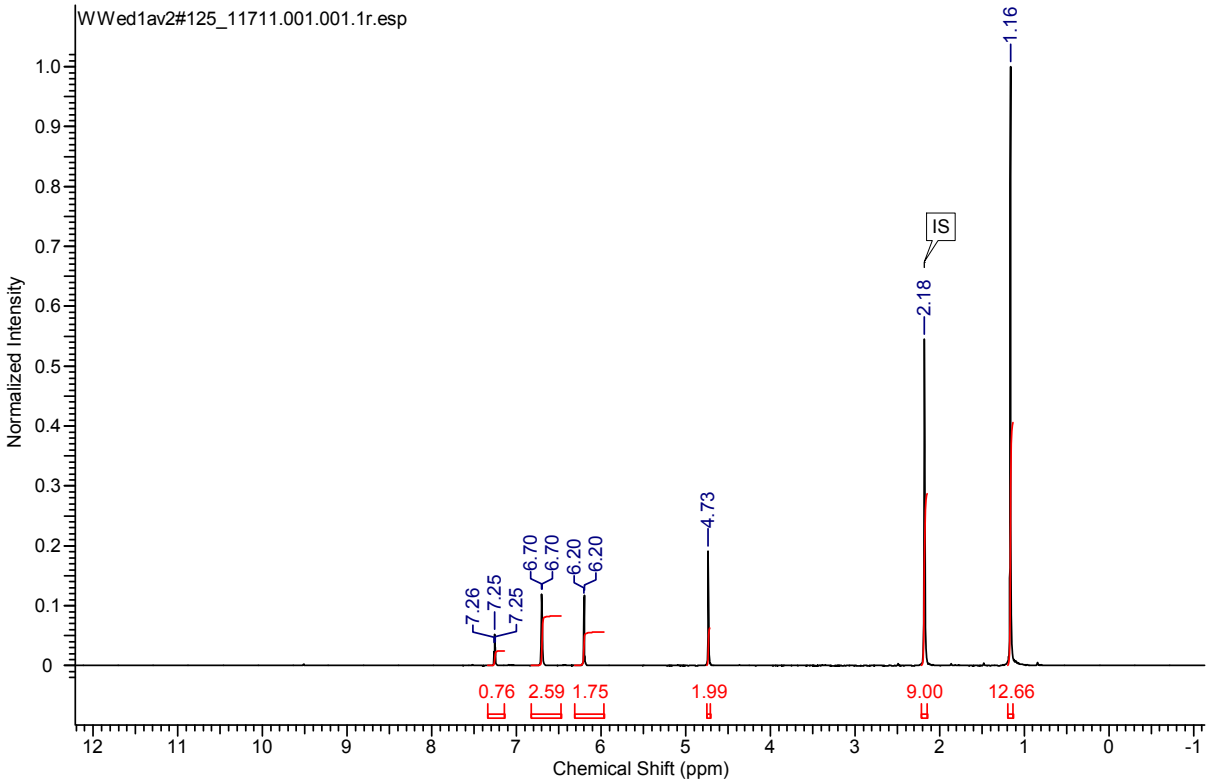
^{1}H NMR Spectrum of **2l** ($CDCl_3$, 200 MHz, 298 K)



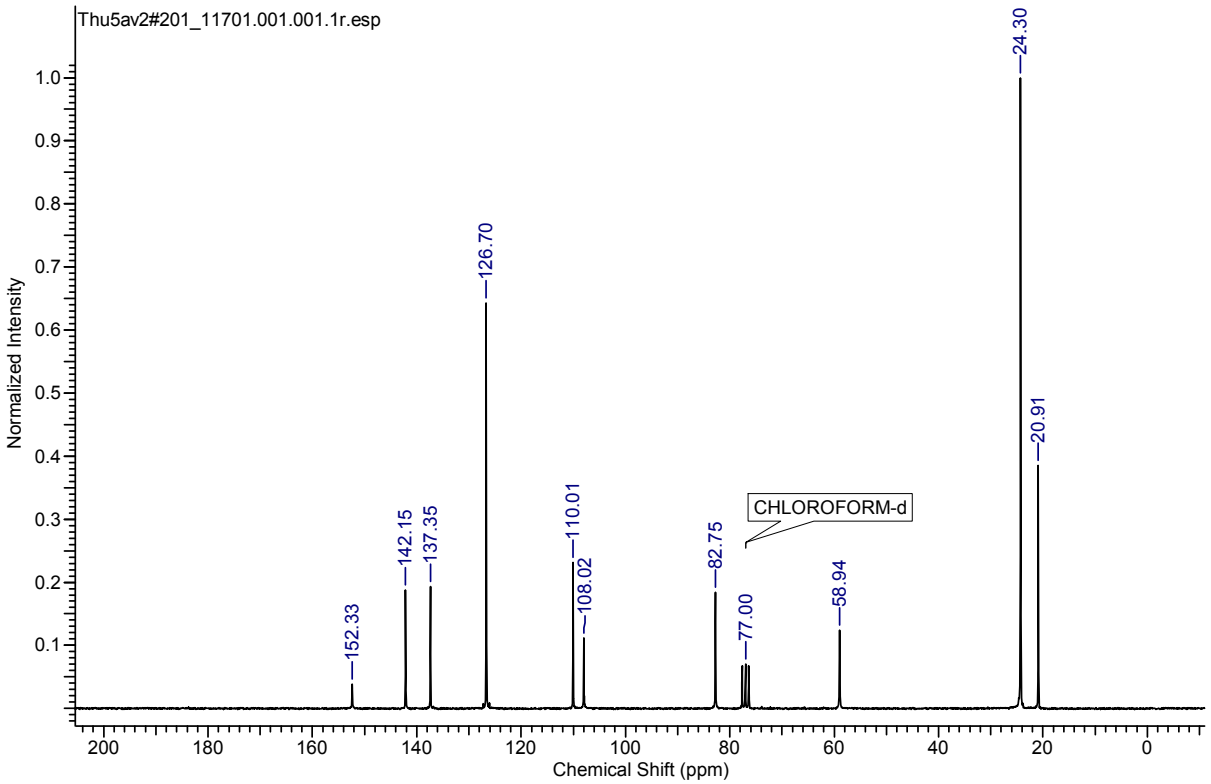
^{13}C NMR spectrum of **2l** ($CDCl_3$, 50.28 MHz, 298 K)



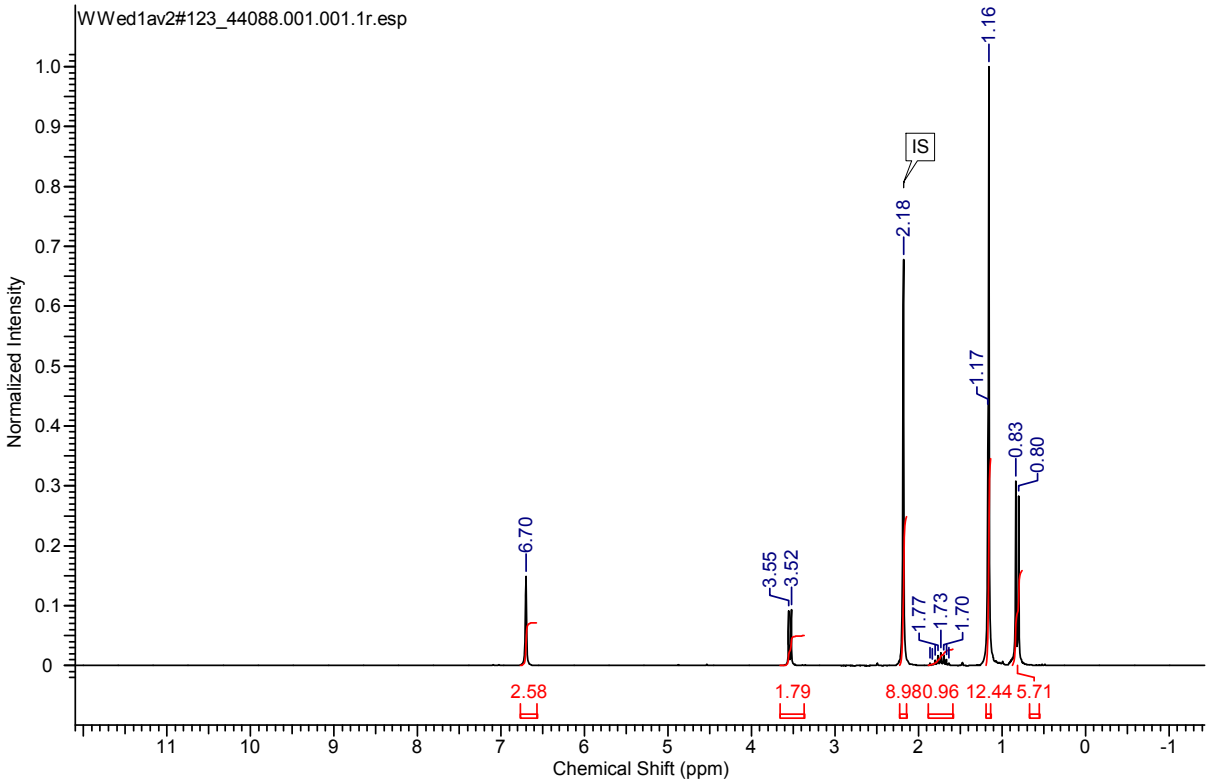
^{1}H NMR Spectrum of **2m** ($CDCl_3$, 200 MHz, 298 K)



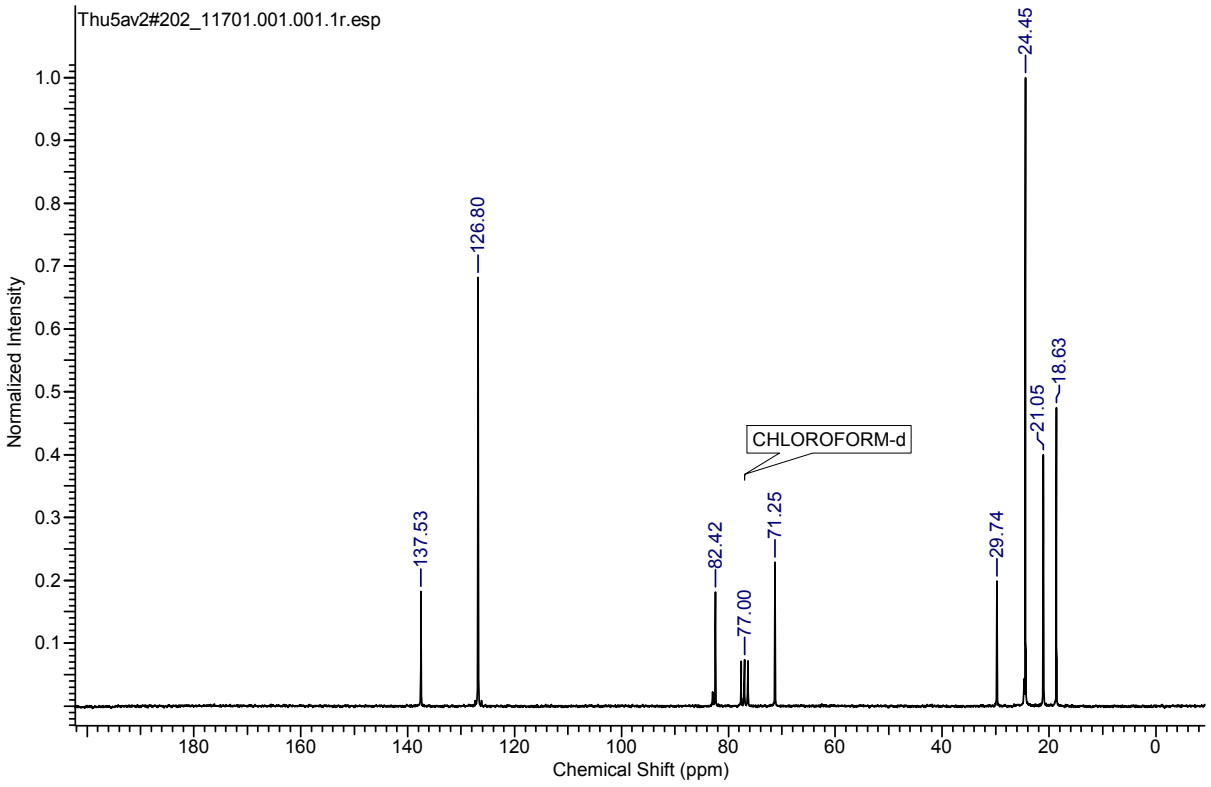
^{13}C NMR spectrum of **2m** ($CDCl_3$, 50.28 MHz, 298 K)



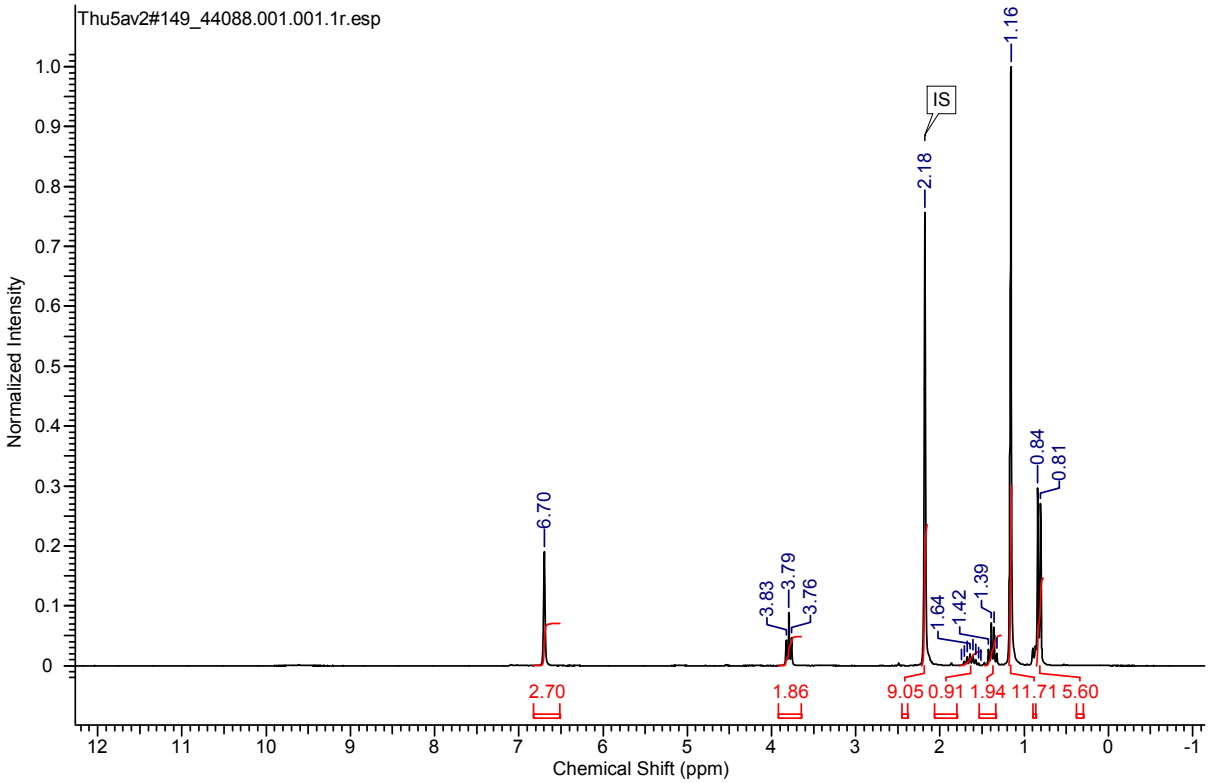
^{1}H NMR Spectrum of **2n** ($CDCl_3$, 200 MHz, 298 K)



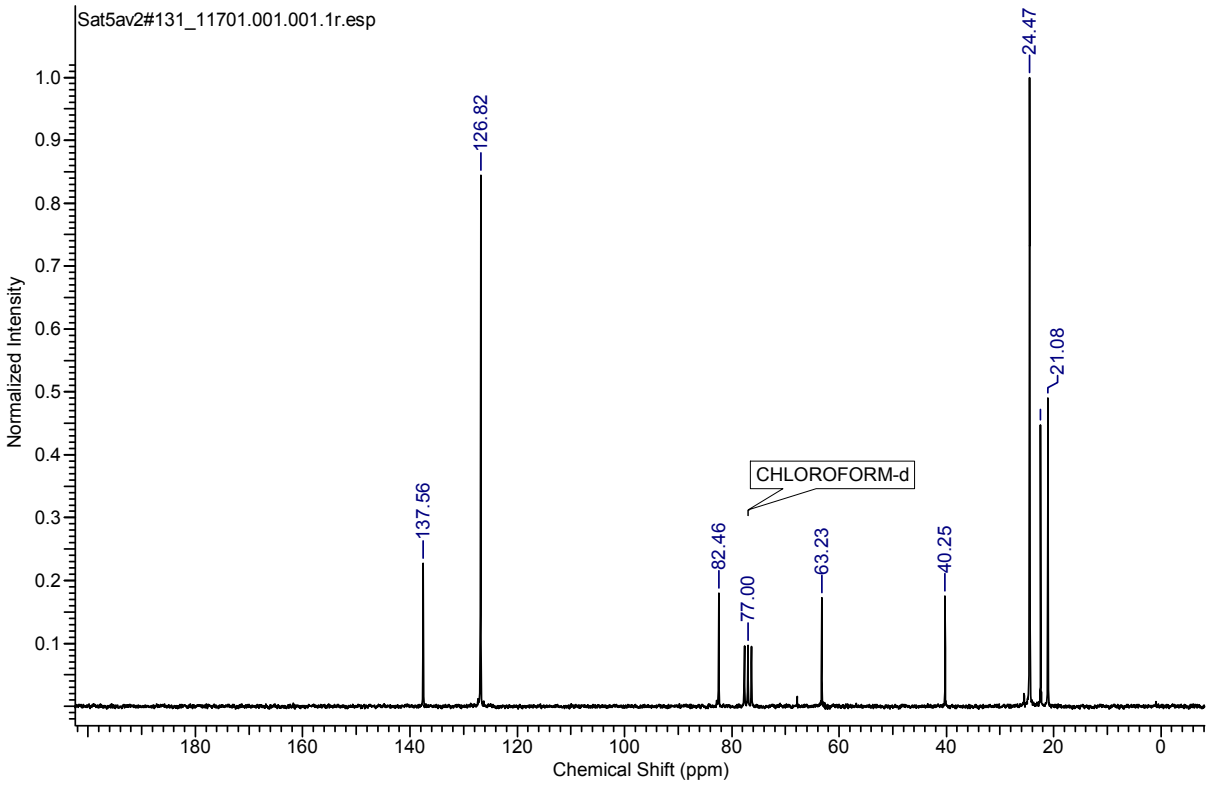
^{13}C NMR spectrum of **2n** ($CDCl_3$, 50.28 MHz, 298 K)



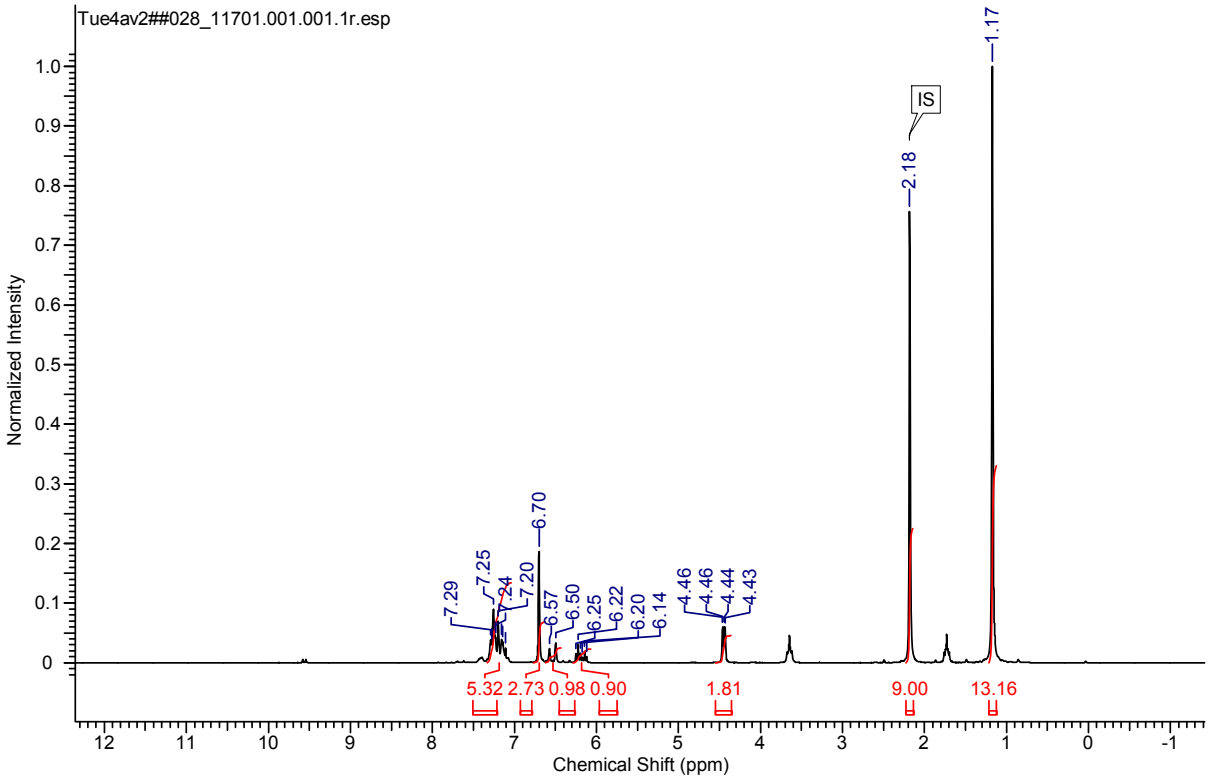
^{1}H NMR Spectrum of **2o** ($CDCl_3$, 200 MHz, 298 K)



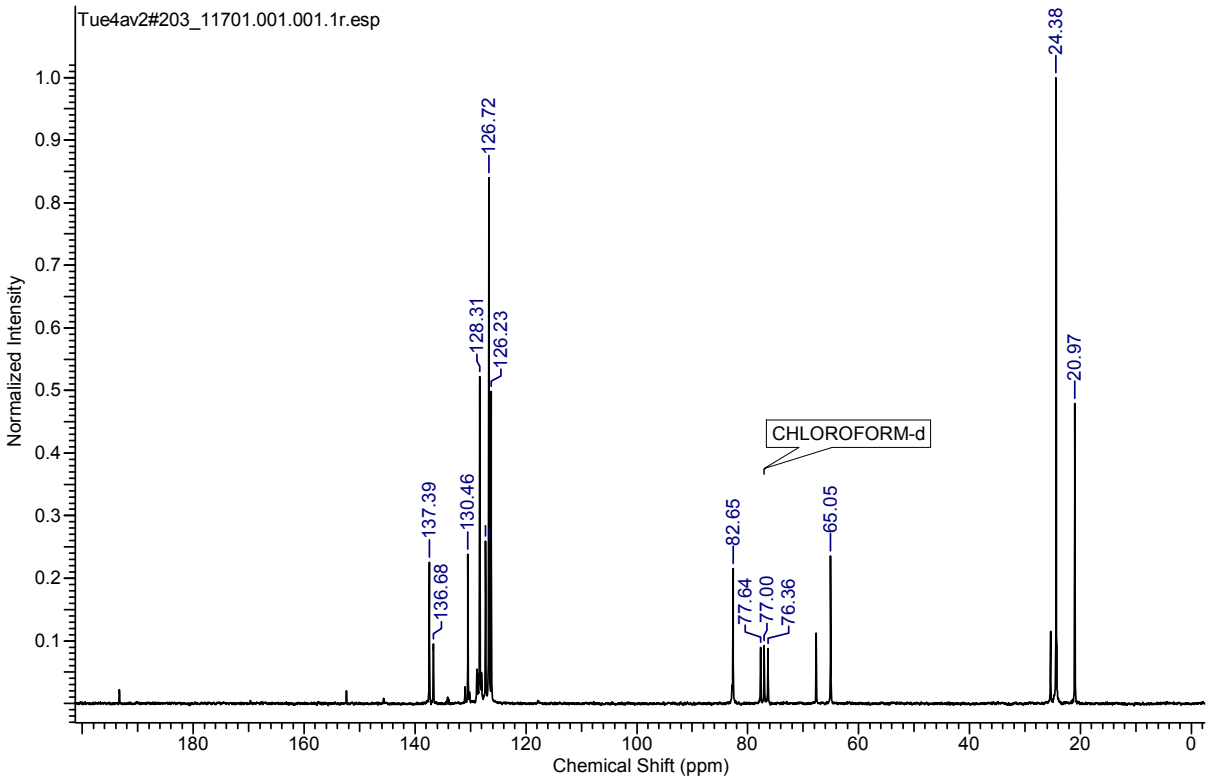
^{13}C NMR spectrum of **2**($CDCl_3$, 50.28 MHz, 298 K)



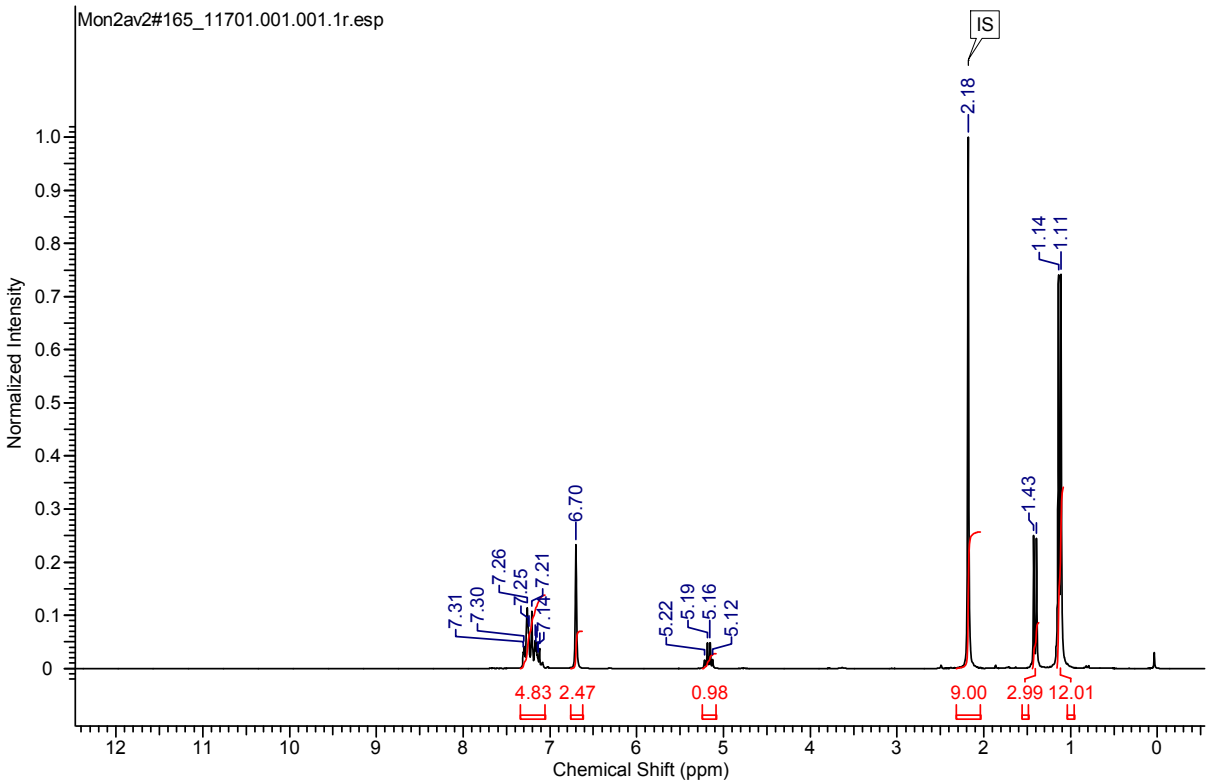
^{1}H NMR Spectrum of **2p** ($CDCl_3$, 200 MHz, 298 K)



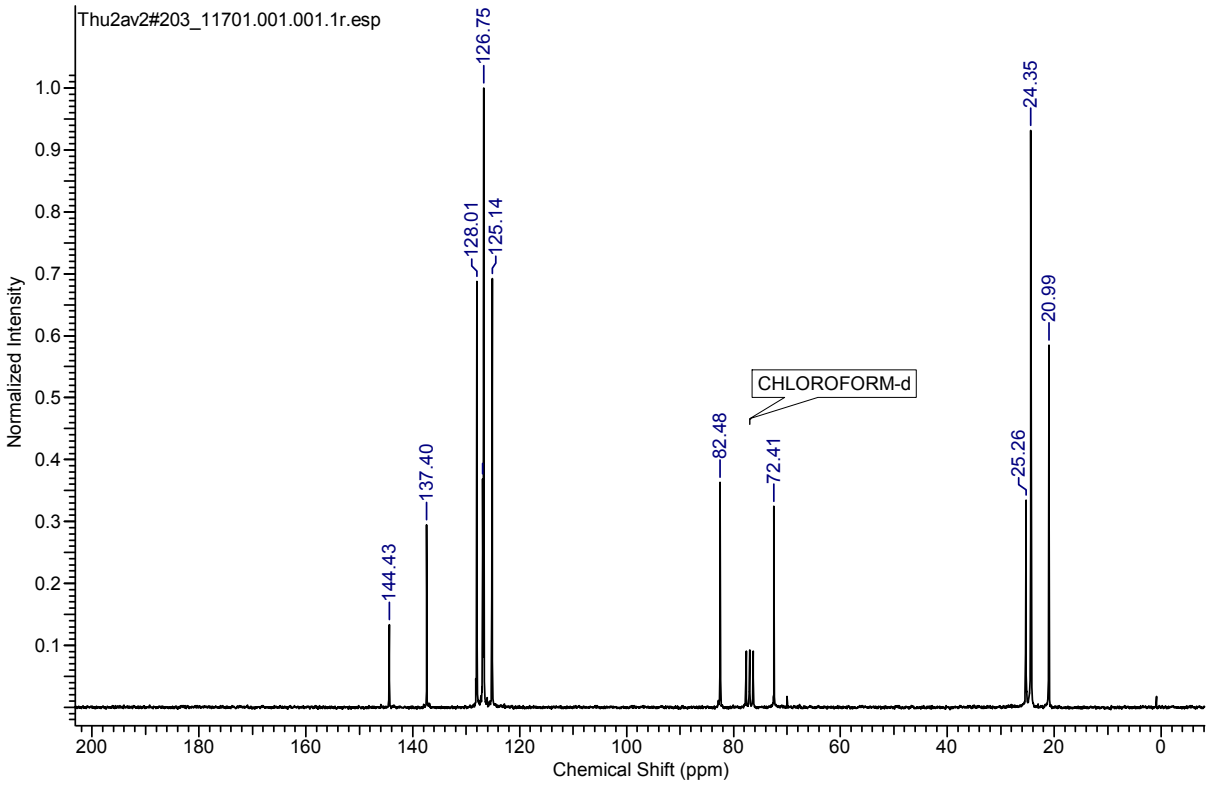
^{13}C NMR spectrum of **2p** ($CDCl_3$, 50.28 MHz, 298 K)



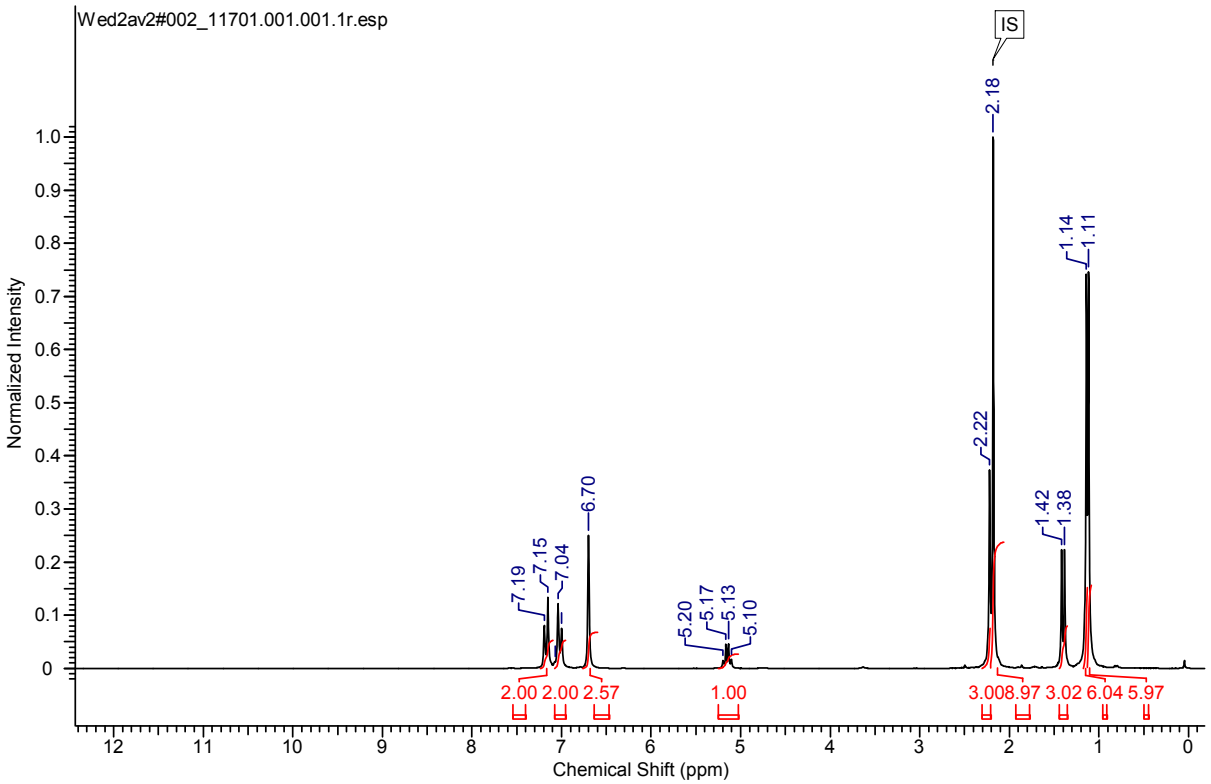
^{1}H NMR Spectrum of **3a** ($CDCl_3$, 200 MHz, 298 K)



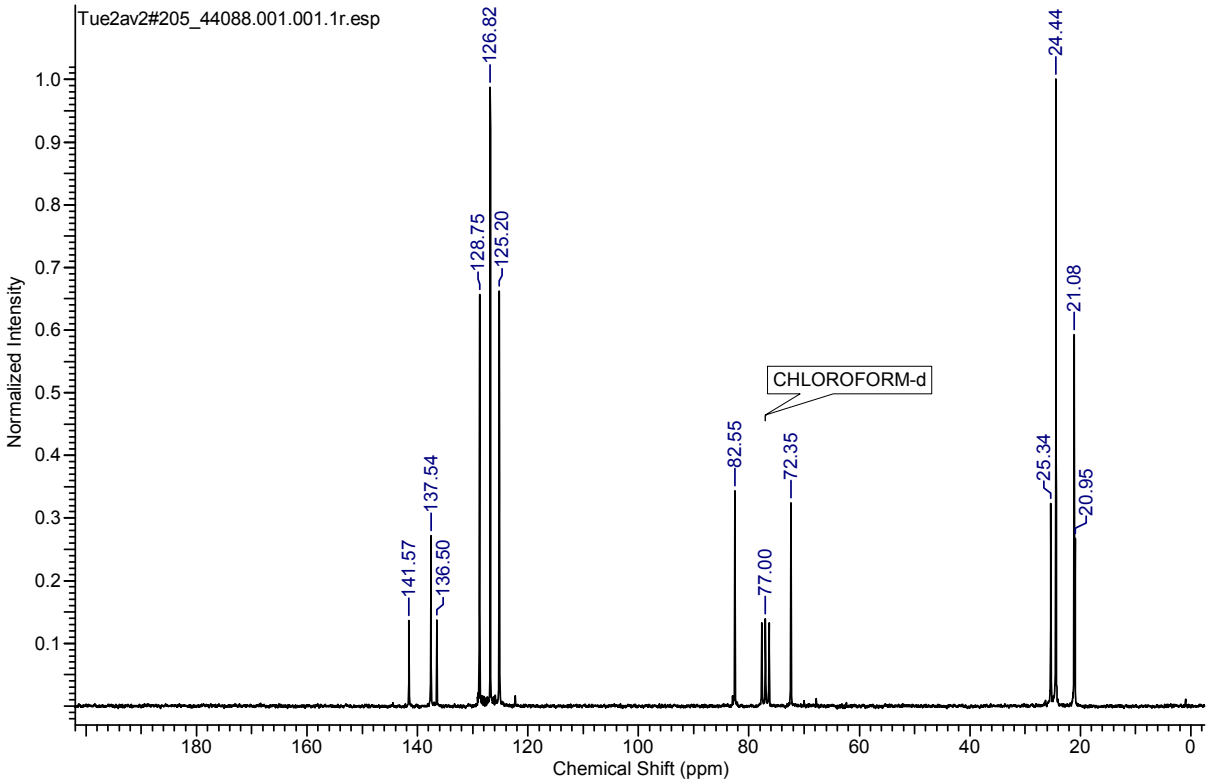
^{13}C NMR spectrum of **3a** ($CDCl_3$, 50.28 MHz, 298 K)



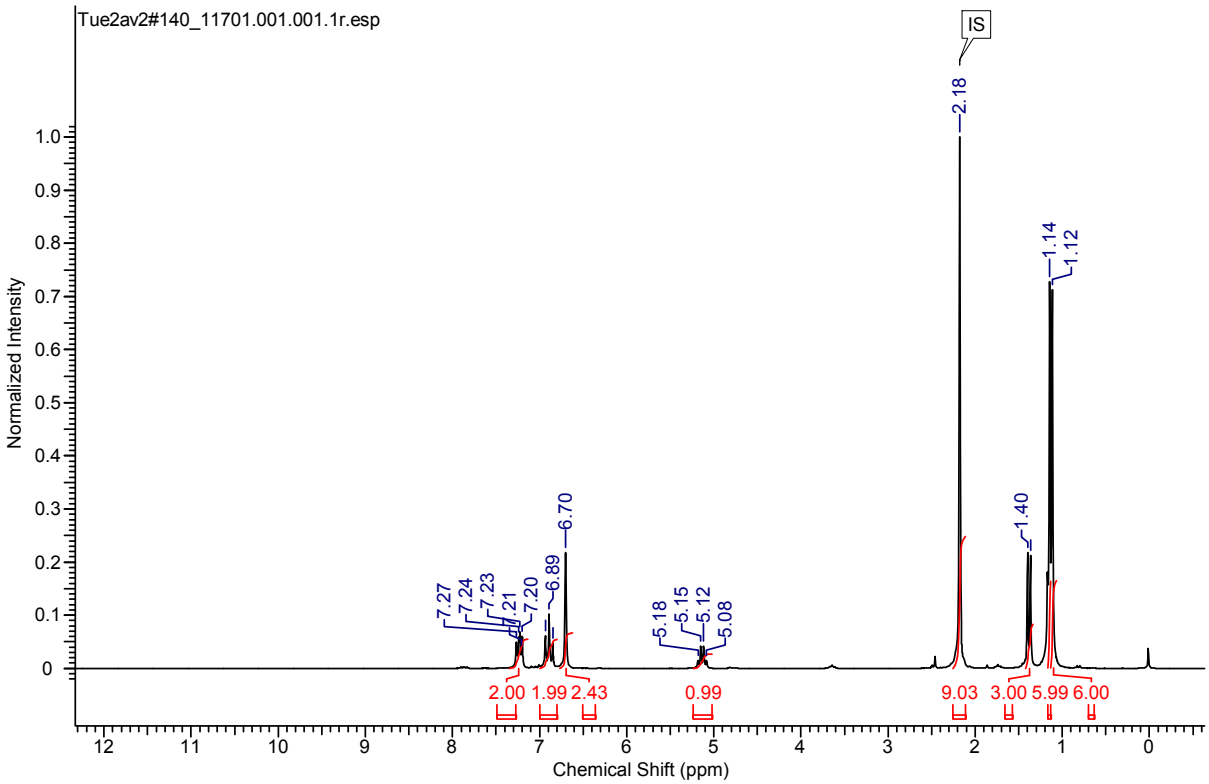
^{1}H NMR Spectrum of **3b** ($CDCl_3$, 200 MHz, 298 K)



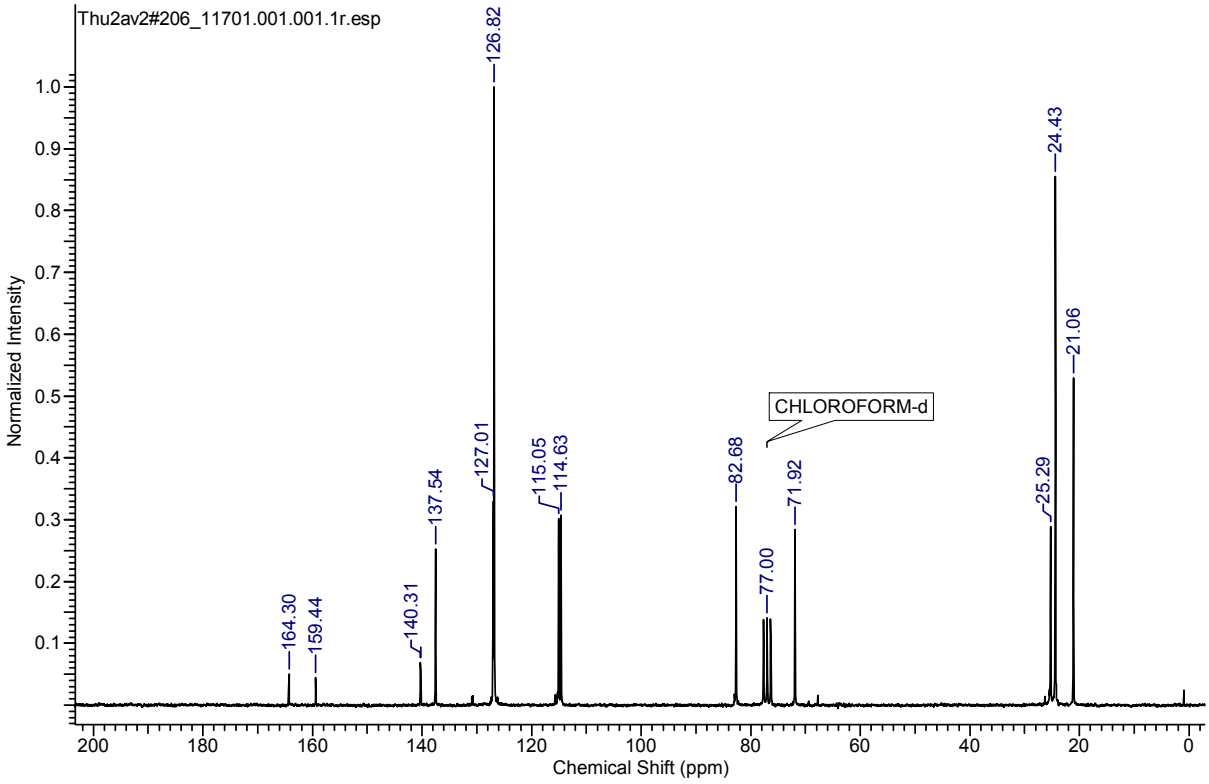
^{13}C NMR spectrum of **3b** ($CDCl_3$, 50.28 MHz, 298 K)



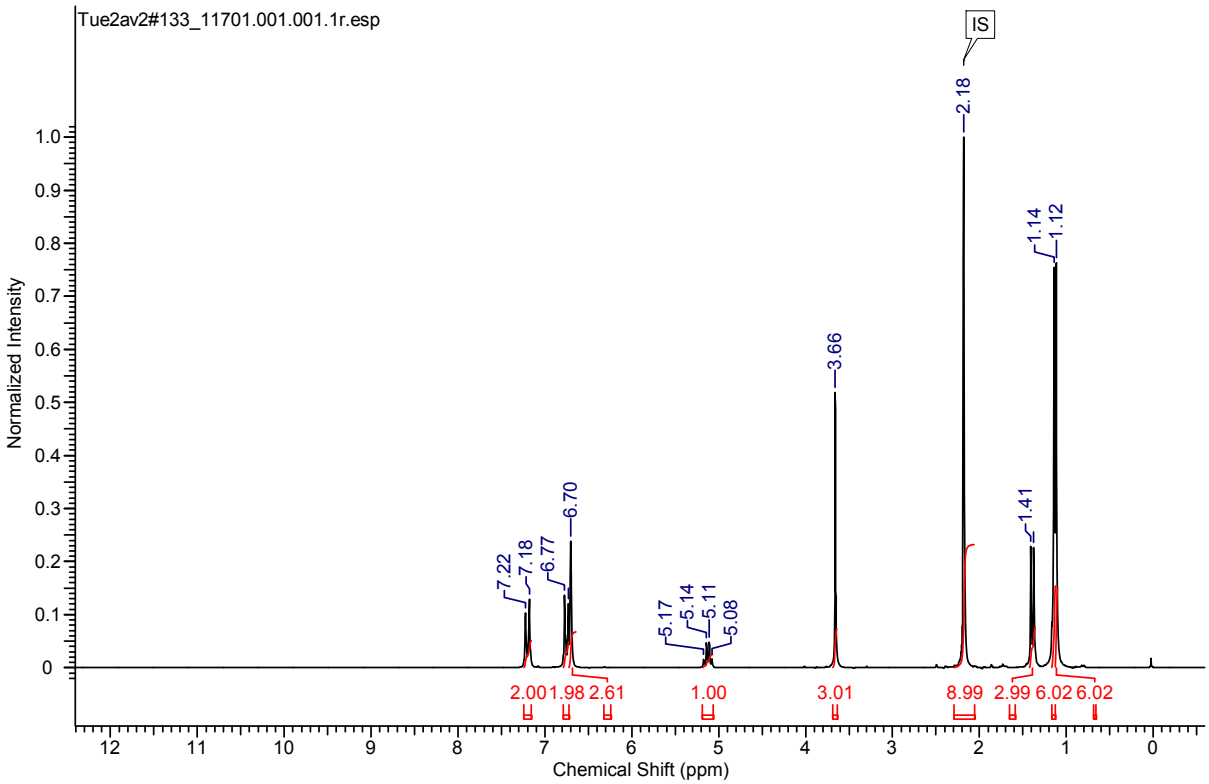
^{1}H NMR Spectrum of **3c** ($CDCl_3$, 200 MHz, 298 K)



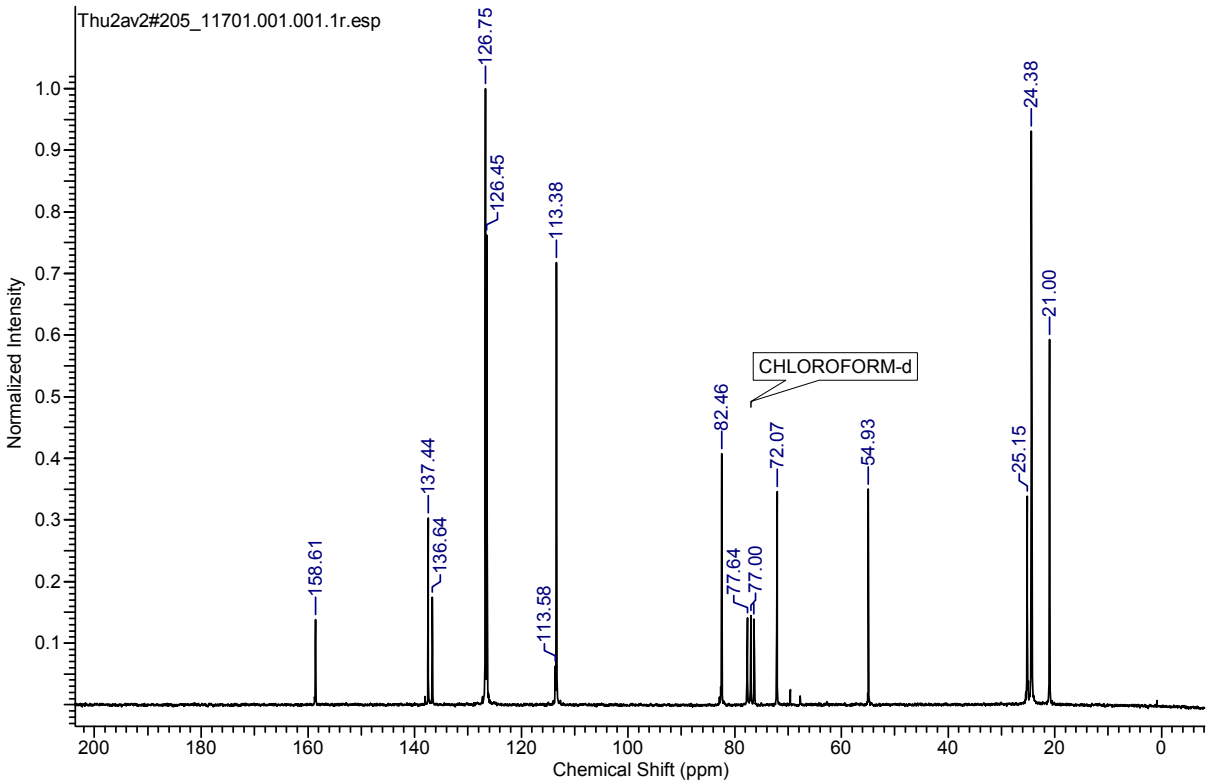
^{13}C NMR spectrum of **3c** ($CDCl_3$, 50.28 MHz, 298 K)



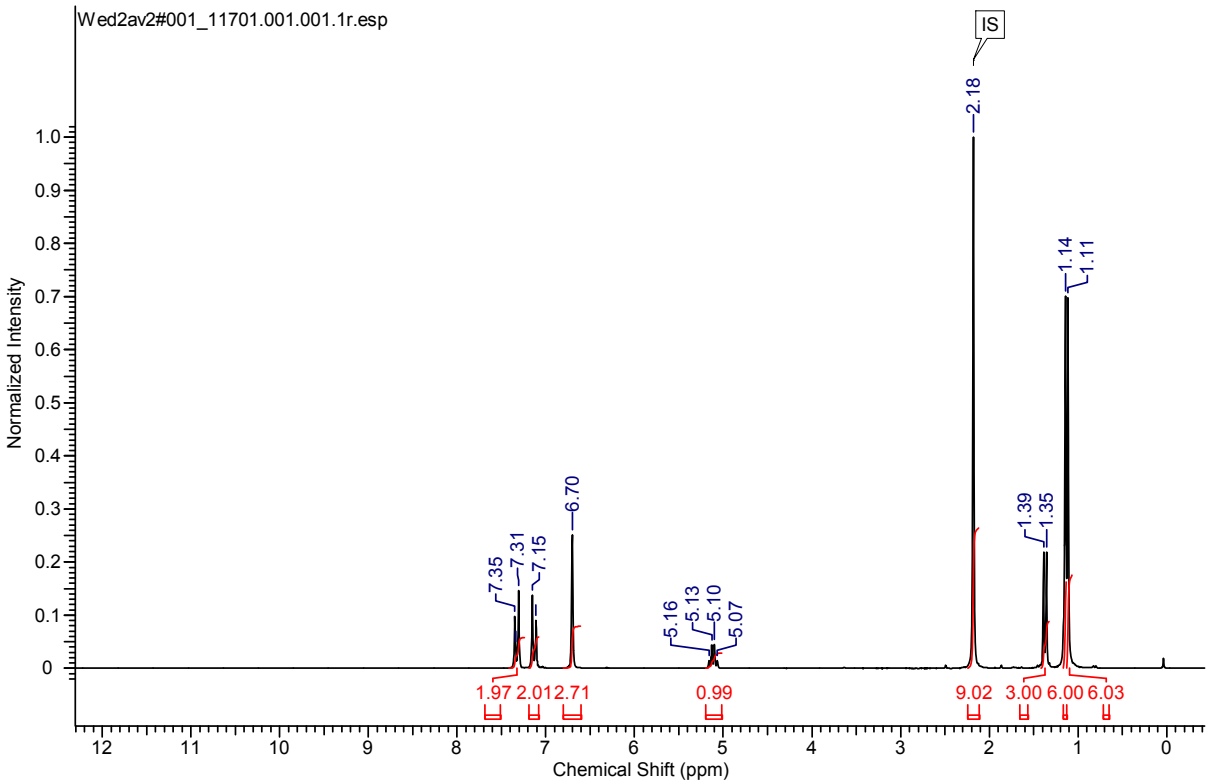
^{1}H NMR Spectrum of **3d** ($CDCl_3$, 200 MHz, 298 K)



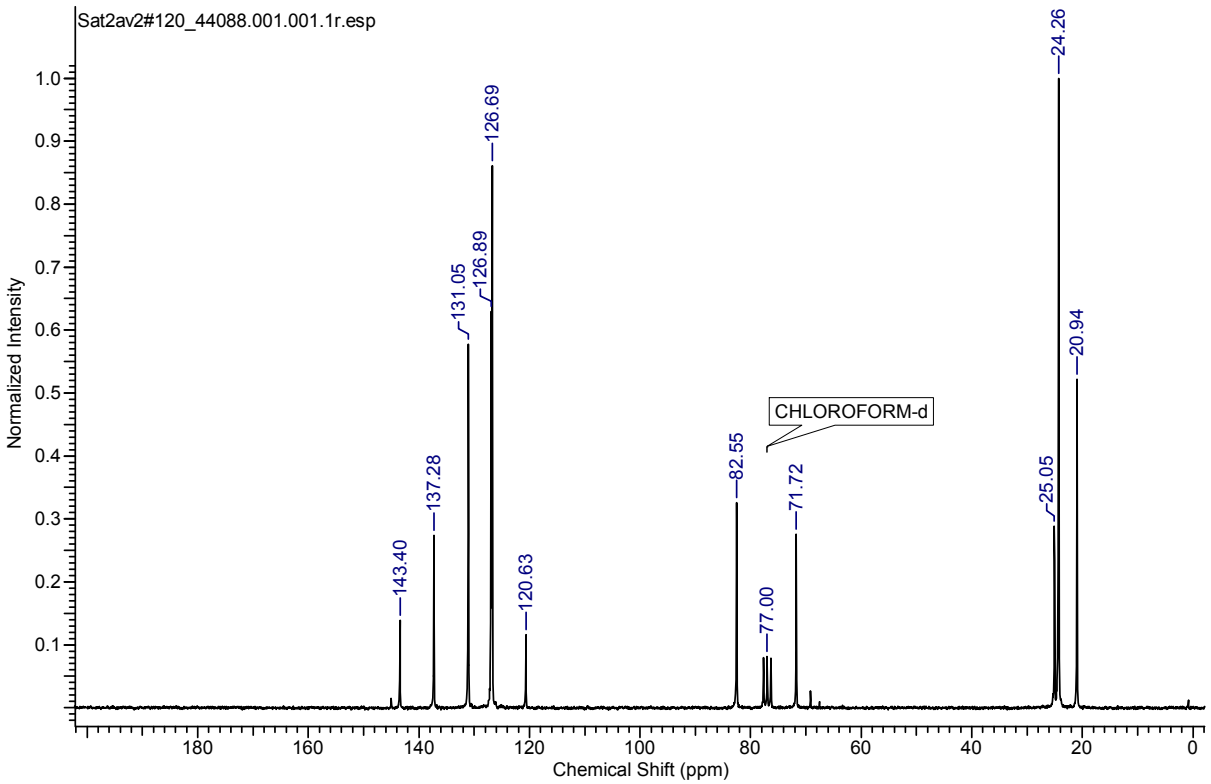
^{13}C NMR spectrum of **3d** ($CDCl_3$, 50.28 MHz, 298 K)



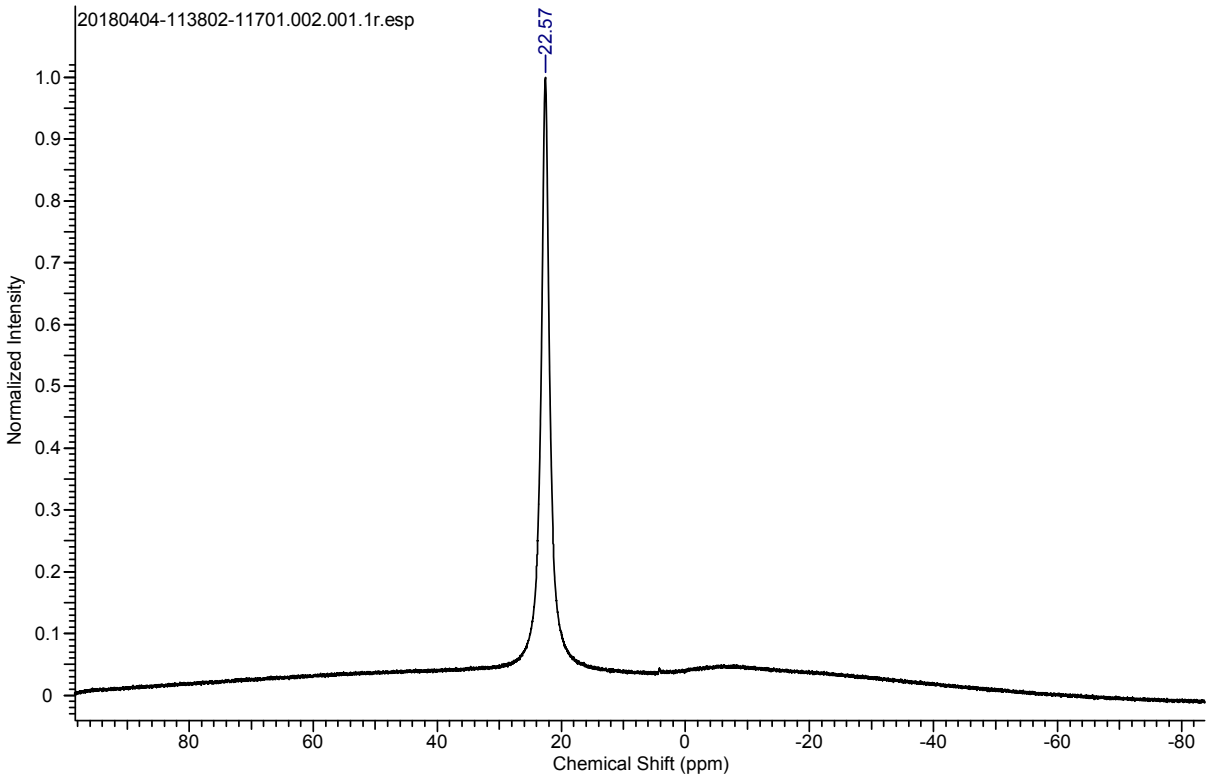
^{1}H NMR Spectrum of **3e** ($CDCl_3$, 200 MHz, 298 K)



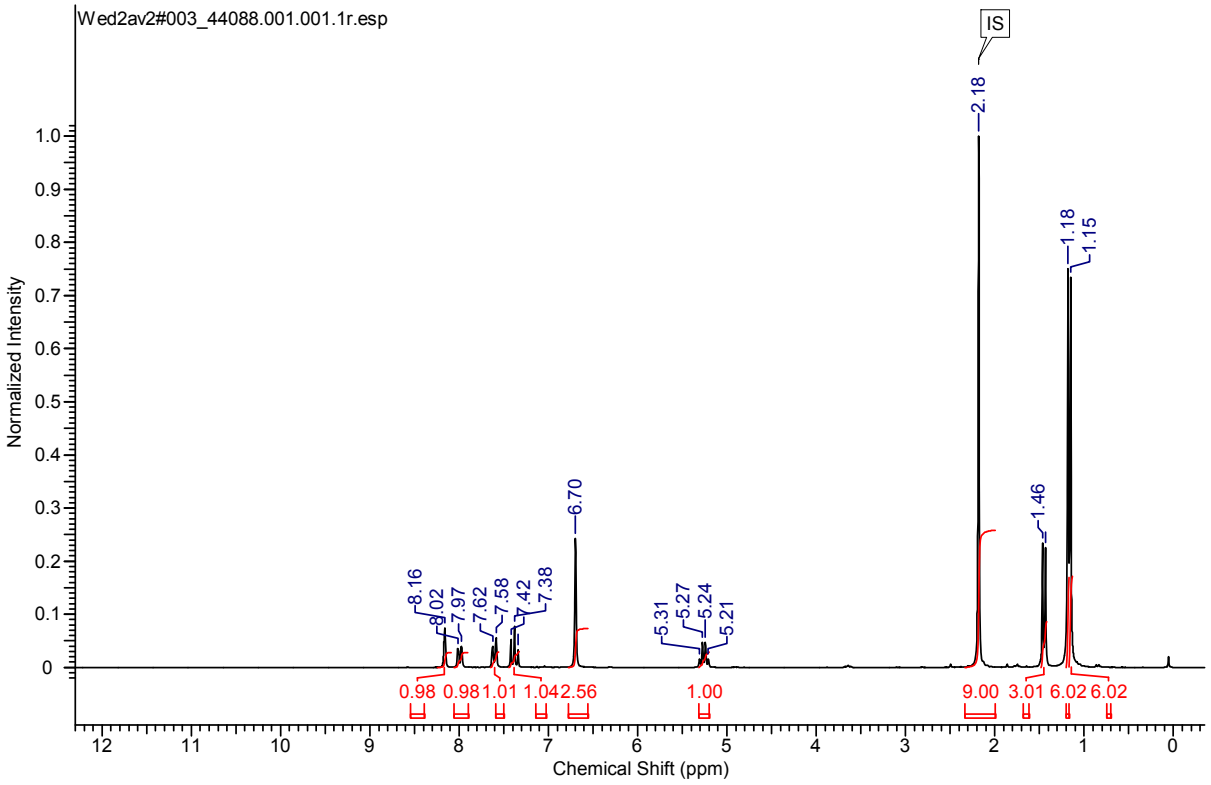
^{13}C NMR spectrum of **3e** ($CDCl_3$, 50.28 MHz, 298 K)



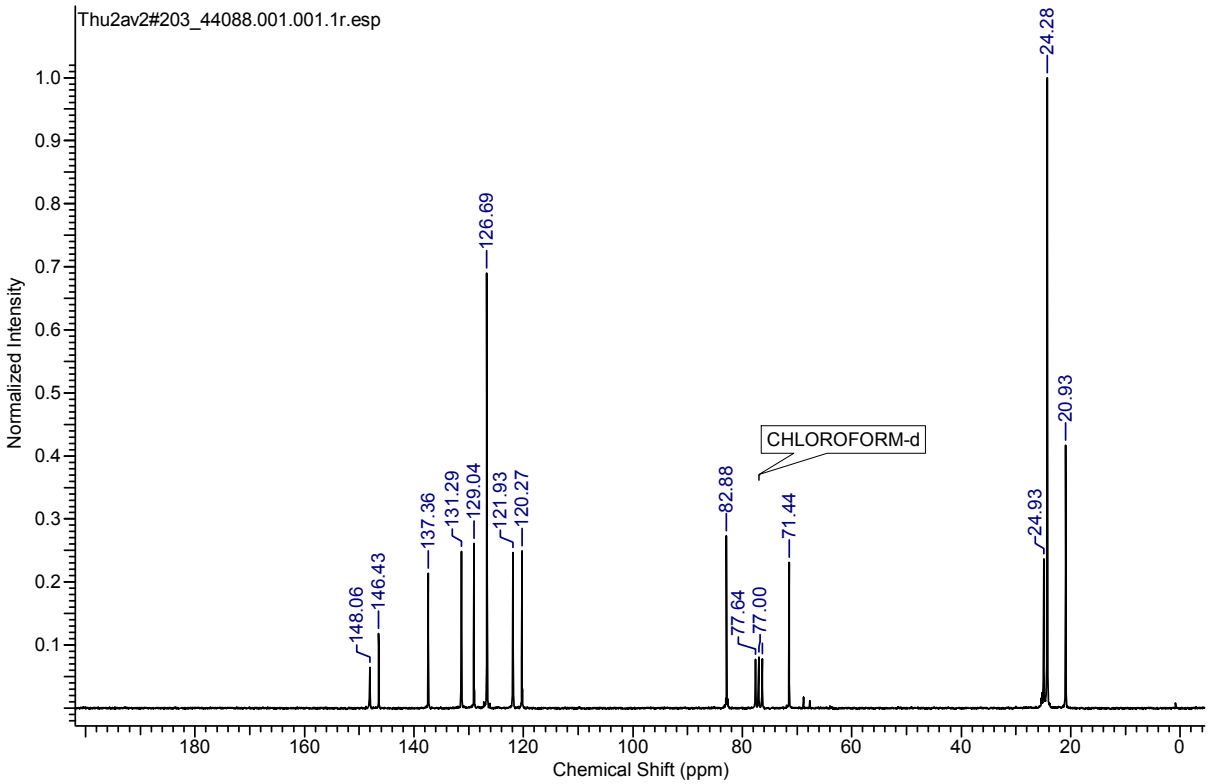
^{11}B NMR spectrum of **3e** (C_6D_6, 128 MHz, 298 K)



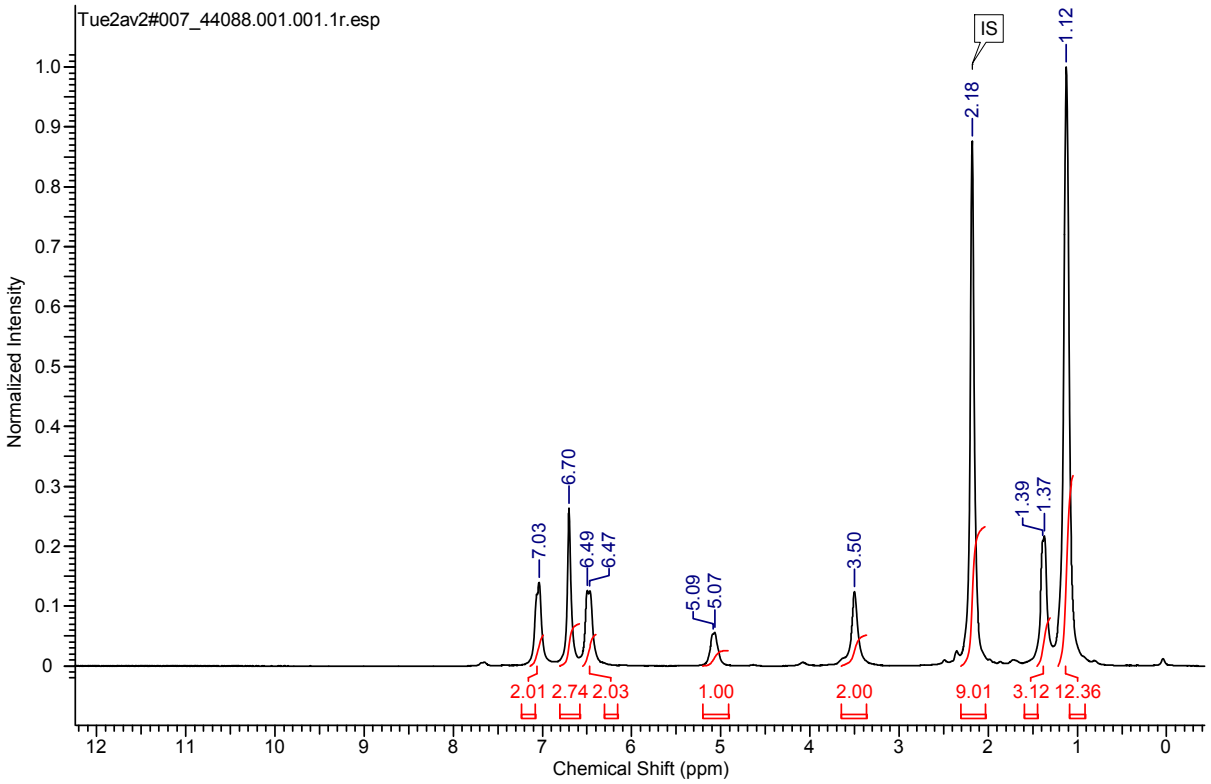
^{1}H NMR Spectrum of **3f** ($CDCl_3$, 200 MHz, 298 K)



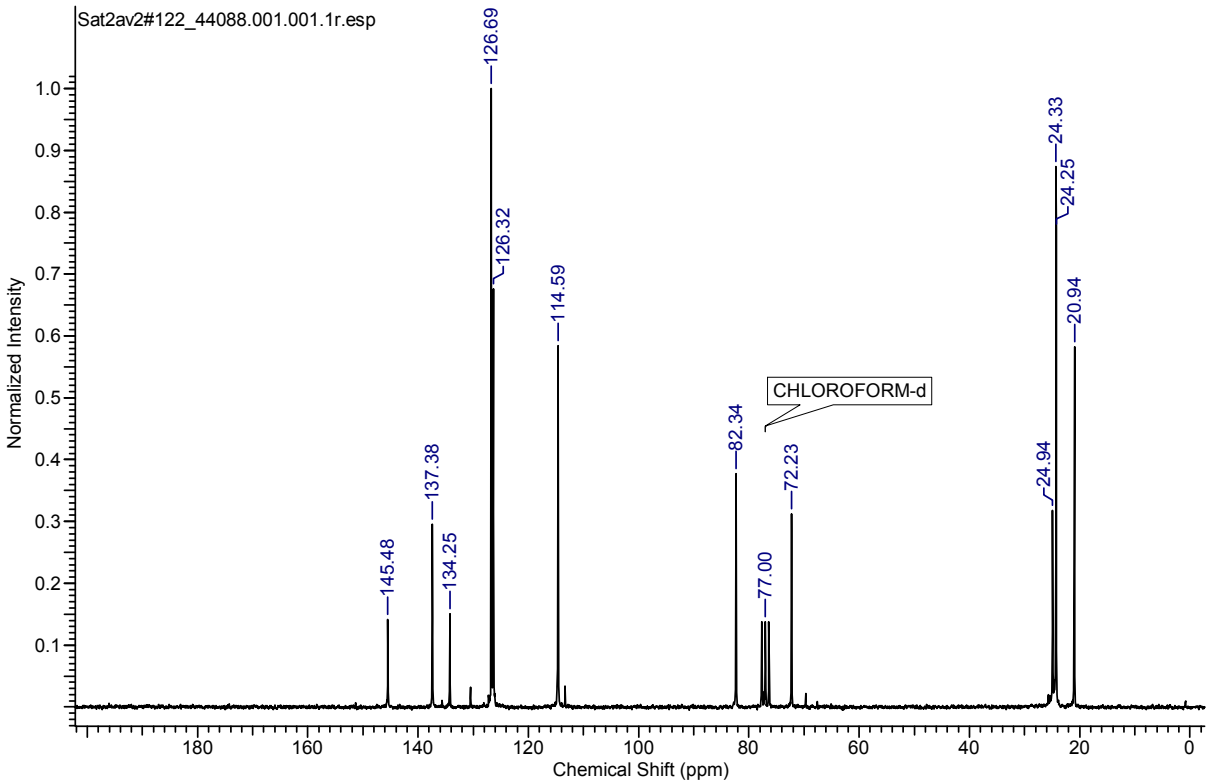
^{13}C NMR spectrum of **3f** ($CDCl_3$, 50.28 MHz, 298 K)



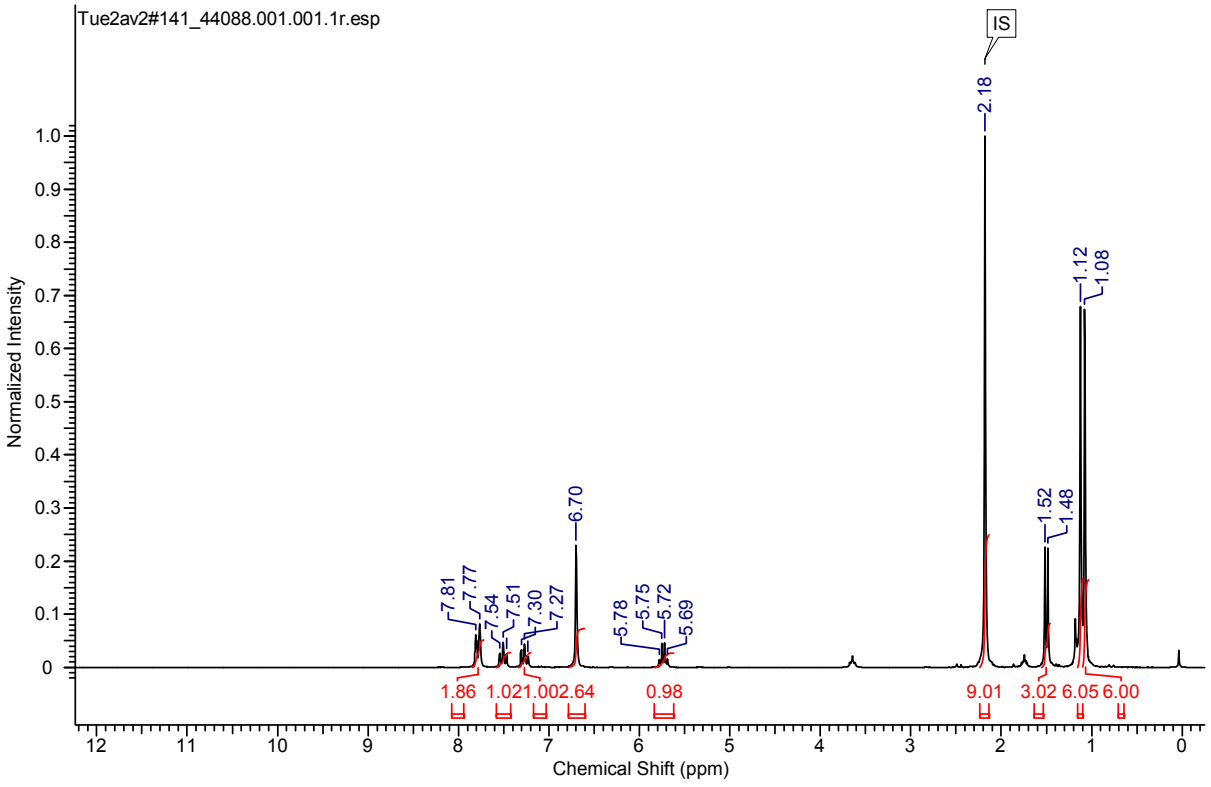
^{1}H NMR Spectrum of **3g** ($CDCl_3$, 200 MHz, 298 K)



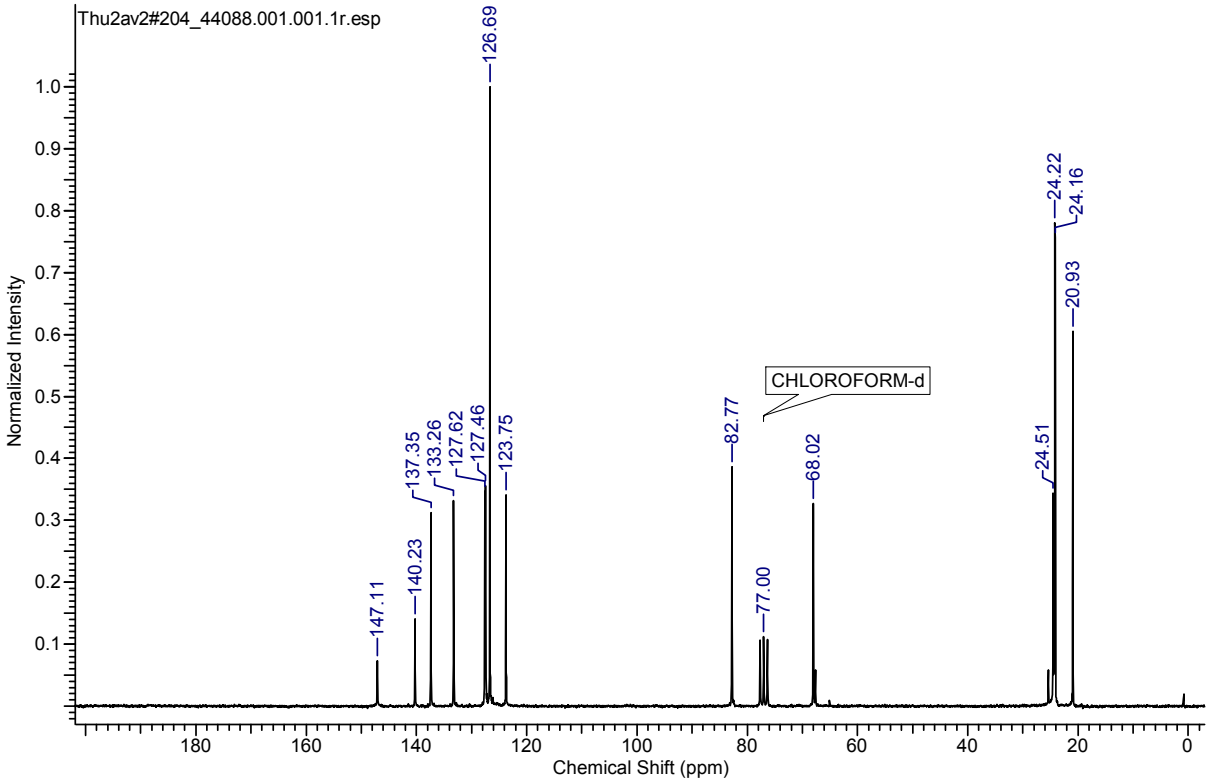
^{13}C NMR spectrum of **3g** ($CDCl_3$, 50.28 MHz, 298 K)



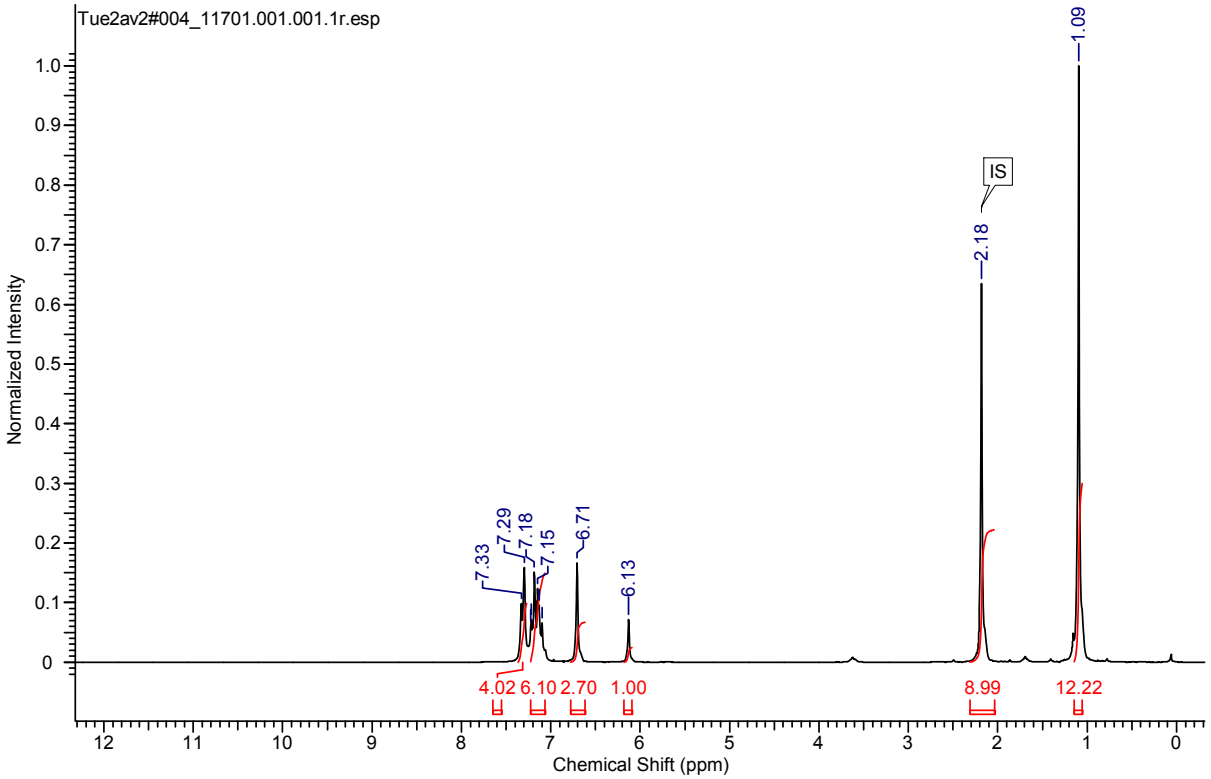
^{1}H NMR Spectrum of **3h** ($CDCl_3$, 200 MHz, 298 K)



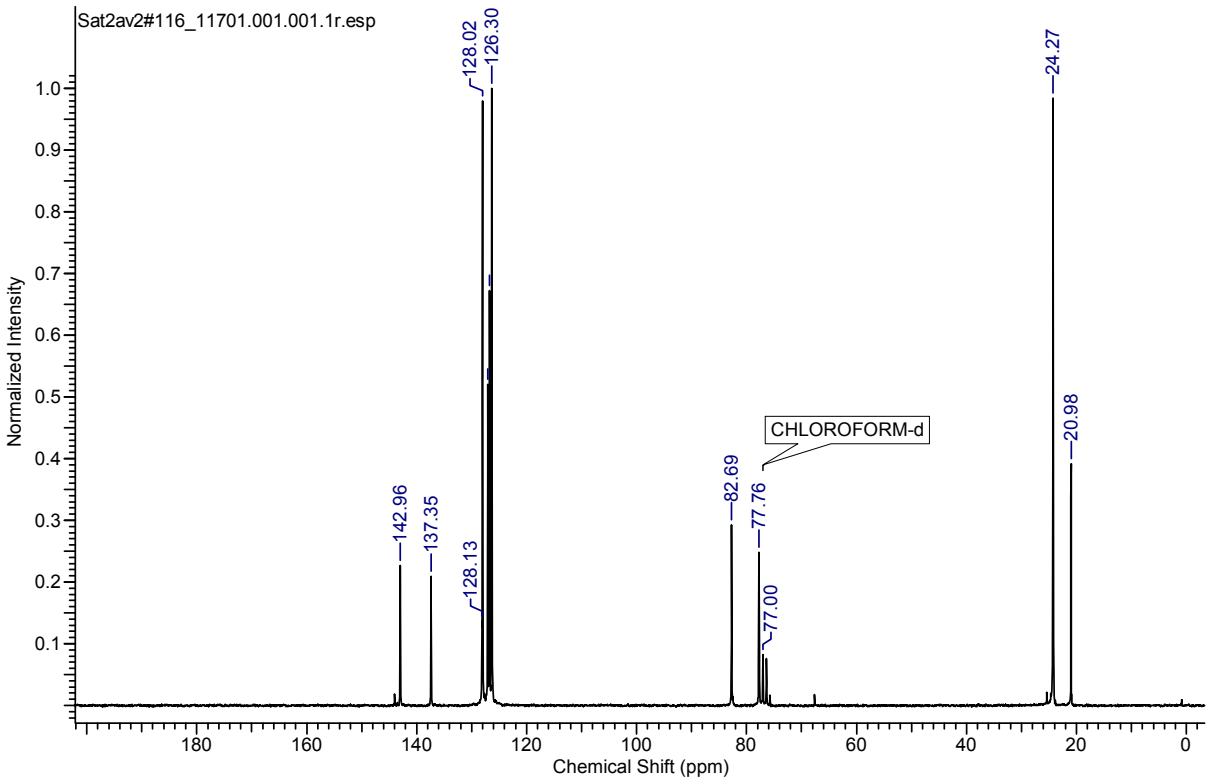
^{13}C NMR spectrum of **3h** ($CDCl_3$, 50.28 MHz, 298 K)



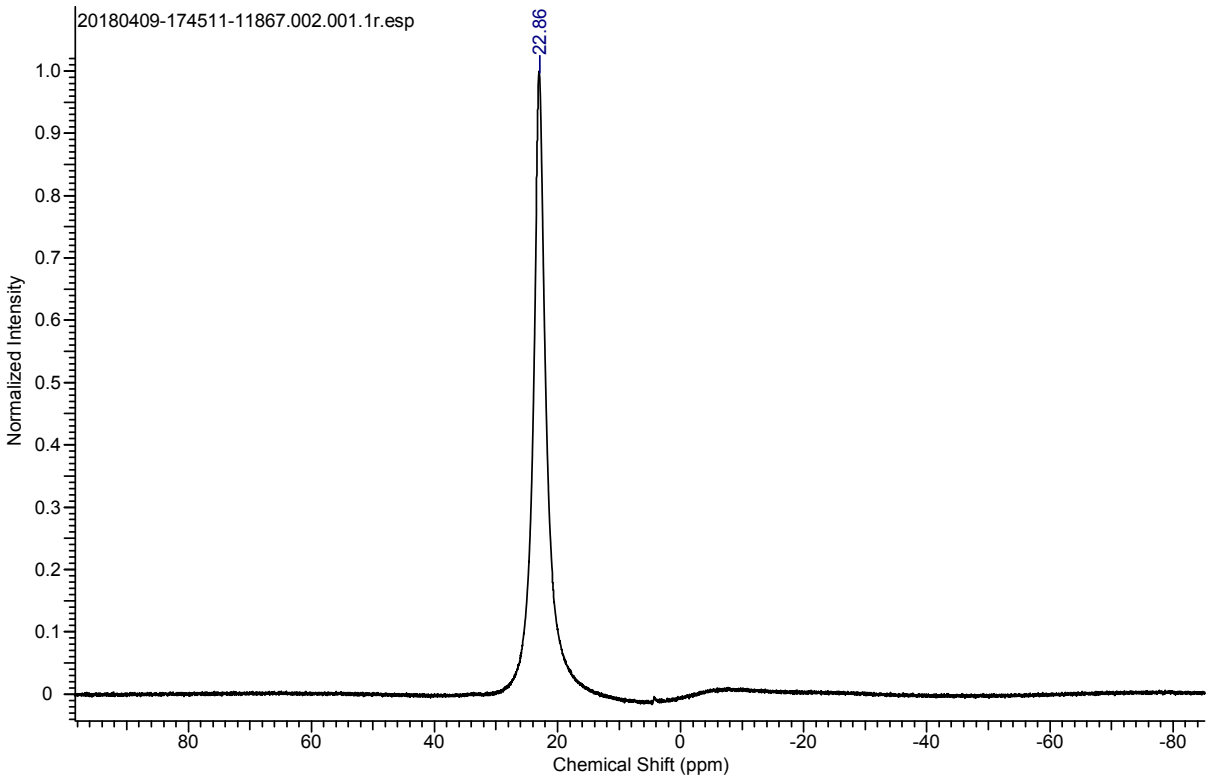
^{1}H NMR Spectrum of **3i** ($CDCl_3$, 200 MHz, 298 K)



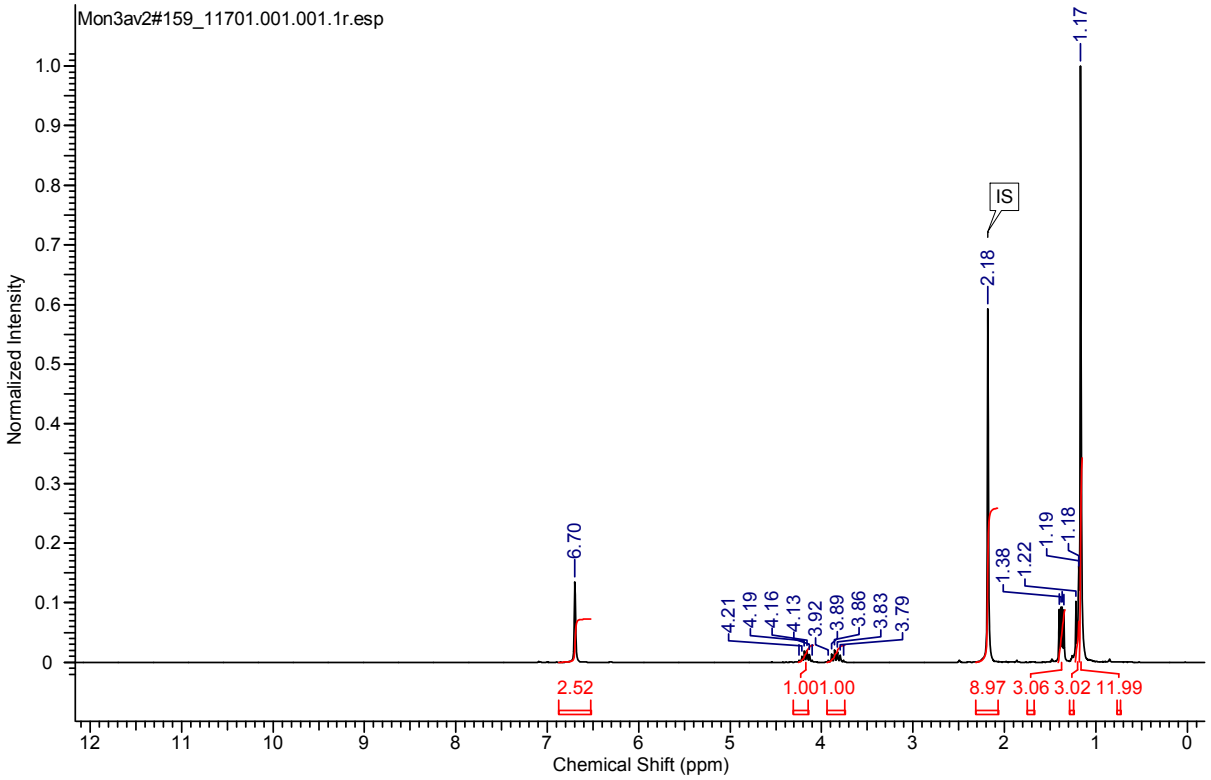
^{13}C NMR spectrum of **3i** ($CDCl_3$, 50.28 MHz, 298 K)



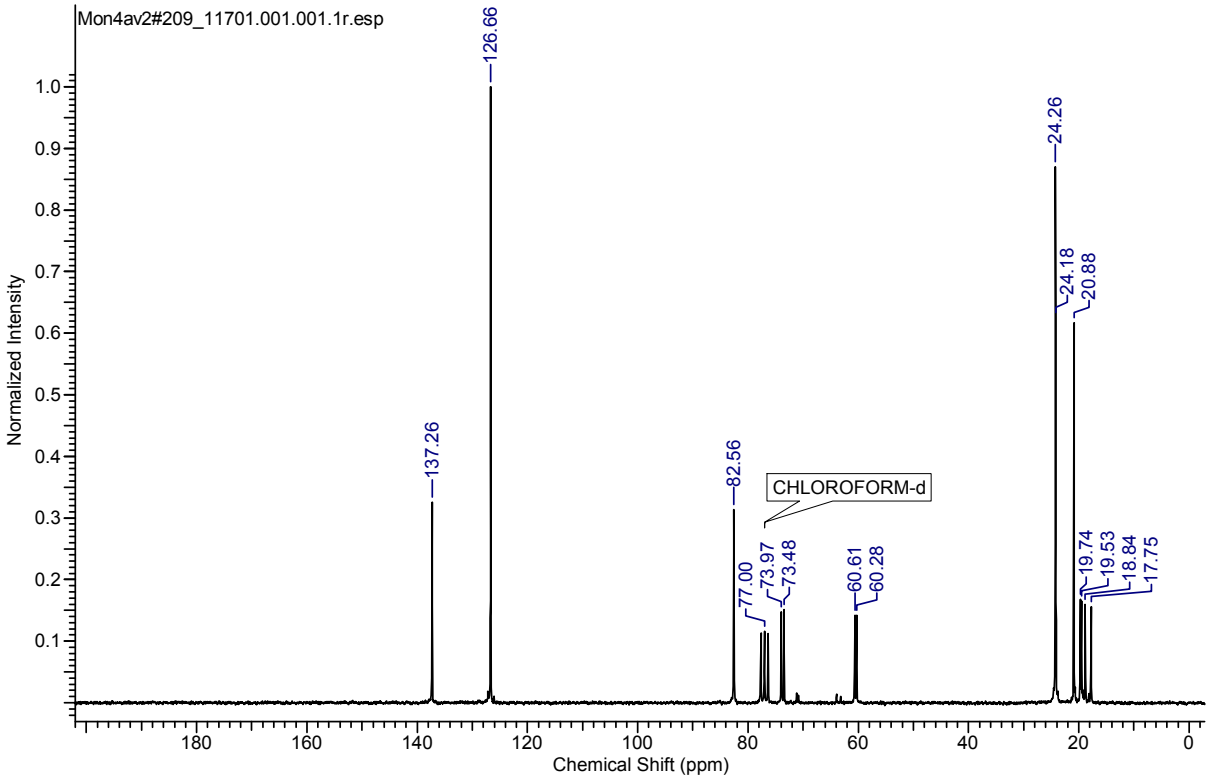
^{11}B NMR spectrum of **3i** (C_6D_6, 128 MHz, 298 K)



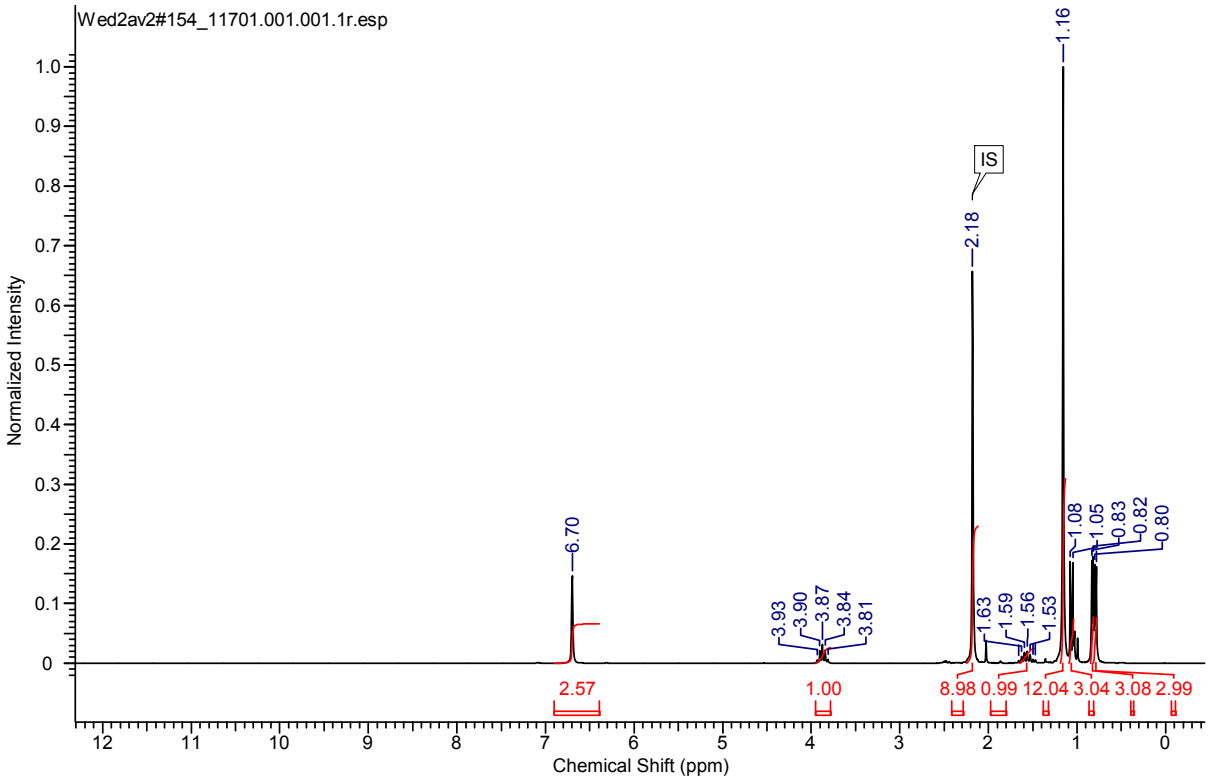
^{1}H NMR Spectrum of **3j** ($CDCl_3$, 200 MHz, 298 K)



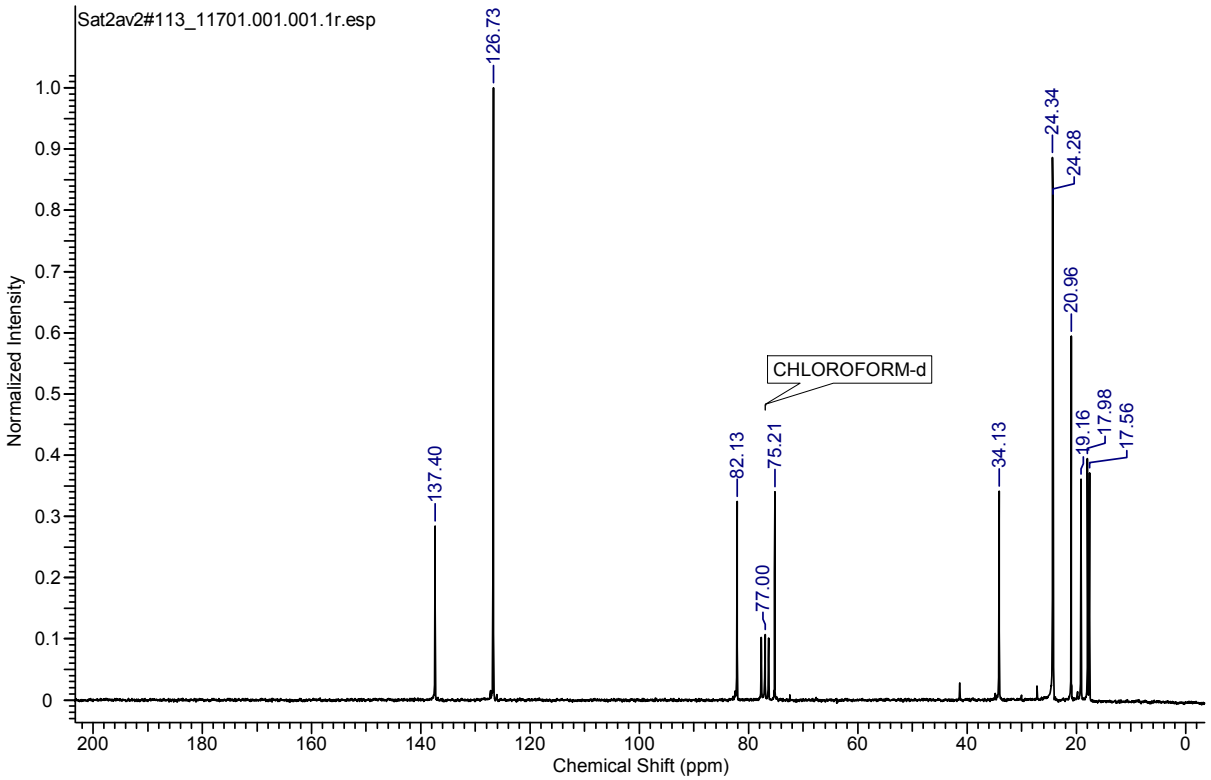
^{13}C NMR spectrum of **3j** ($CDCl_3$, 50.28 MHz, 298 K)



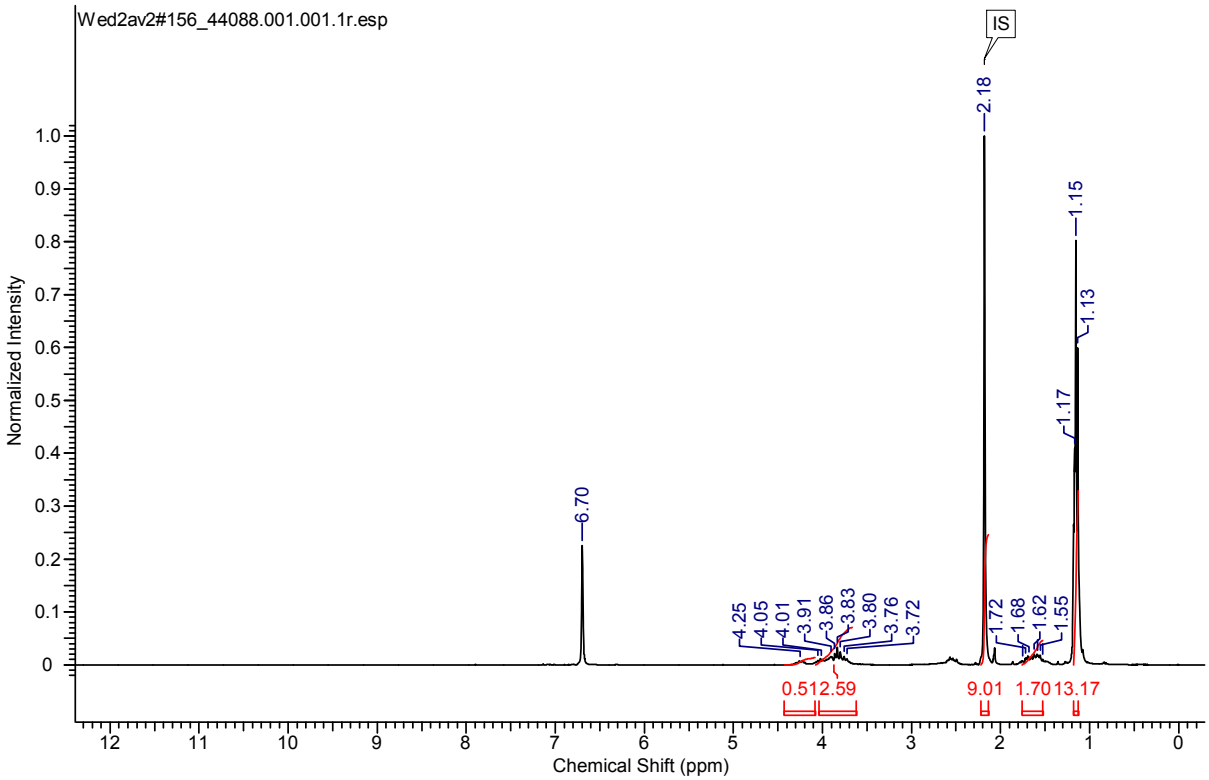
^{1}H NMR Spectrum of **3k** ($CDCl_3$, 200 MHz, 298 K)



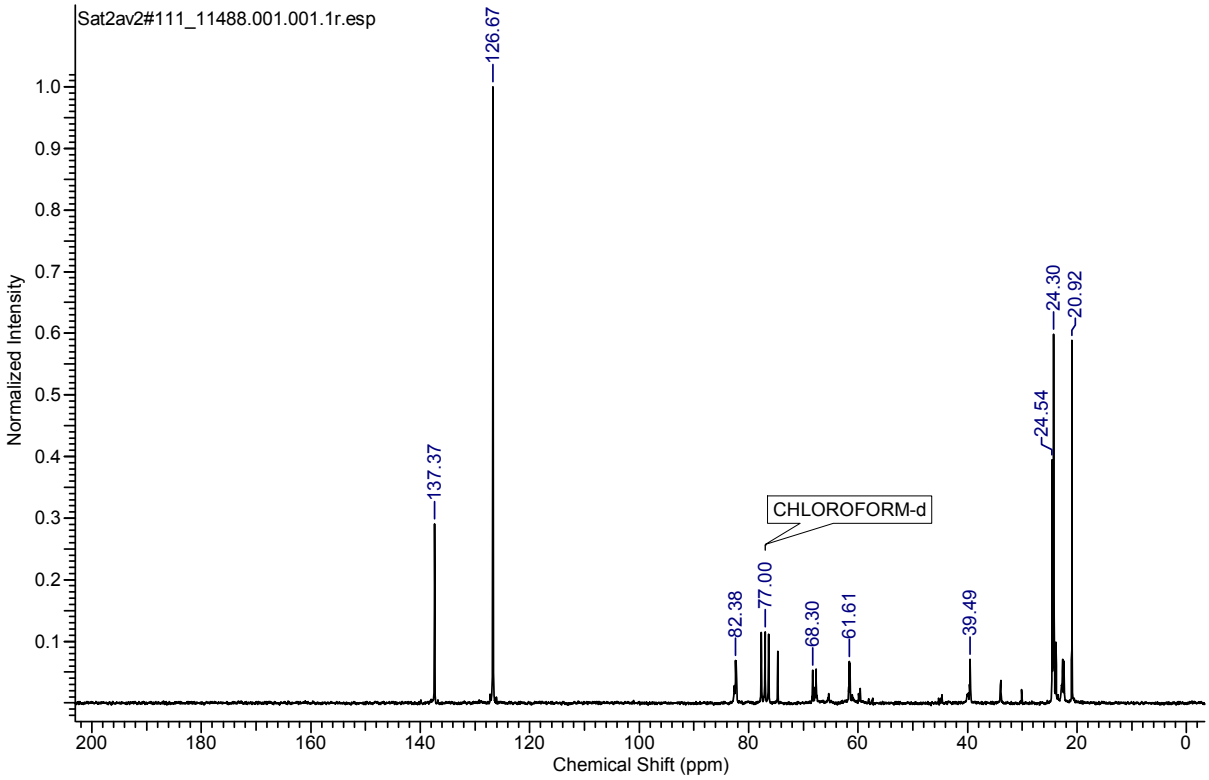
^{13}C NMR spectrum of **3k** ($CDCl_3$, 50.28 MHz, 298 K)



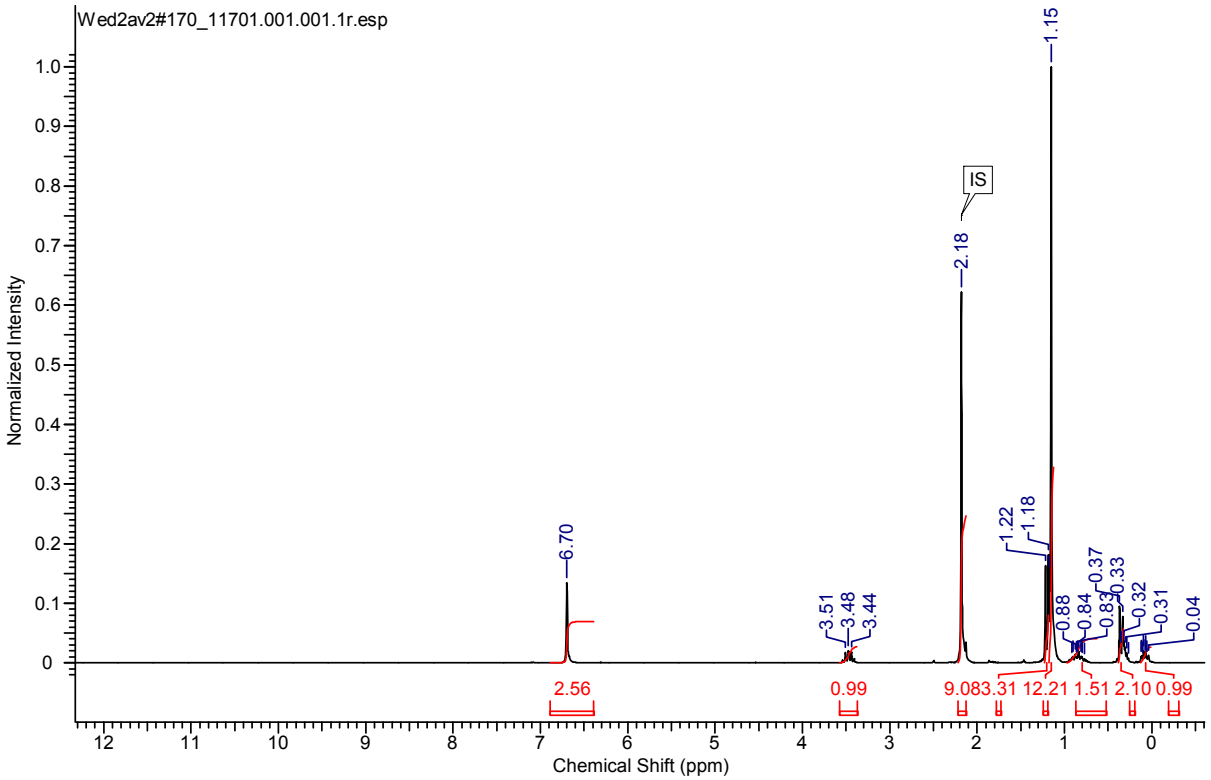
^{1}H NMR Spectrum of **3l** ($CDCl_3$, 200 MHz, 298 K)



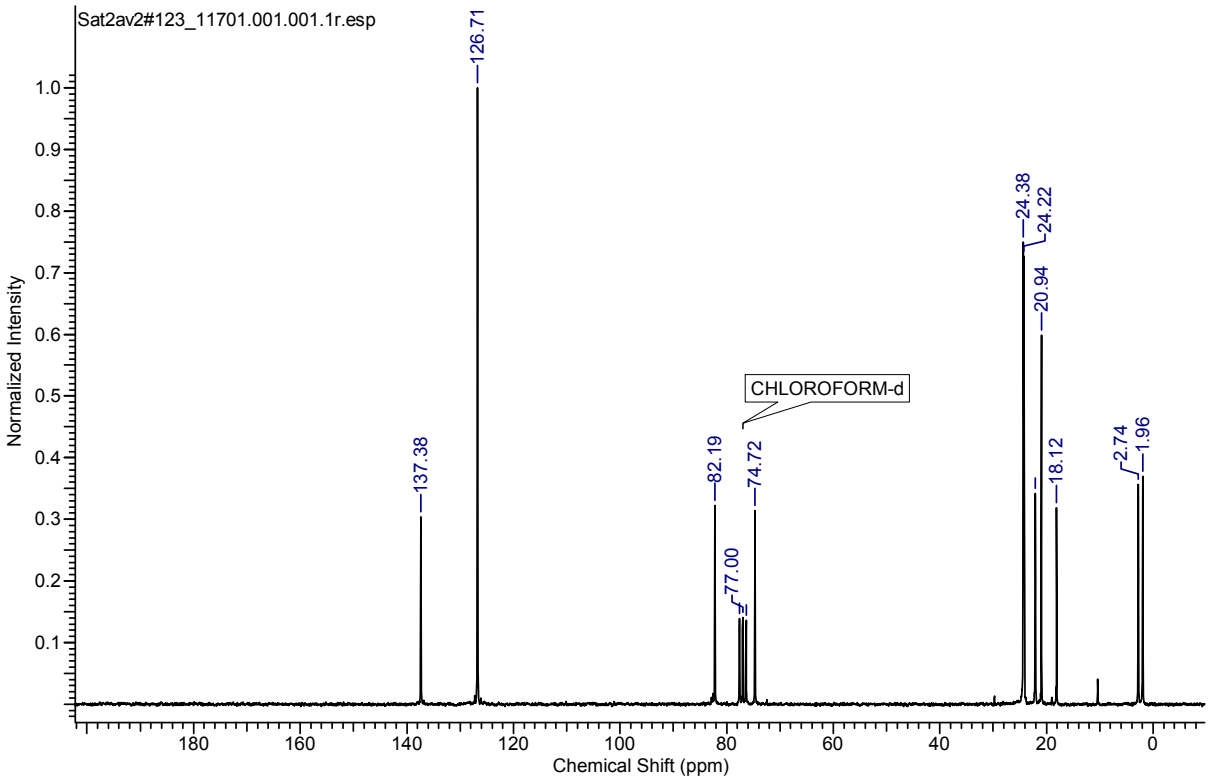
^{13}C NMR spectrum of **3l** ($CDCl_3$, 50.28 MHz, 298 K)



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

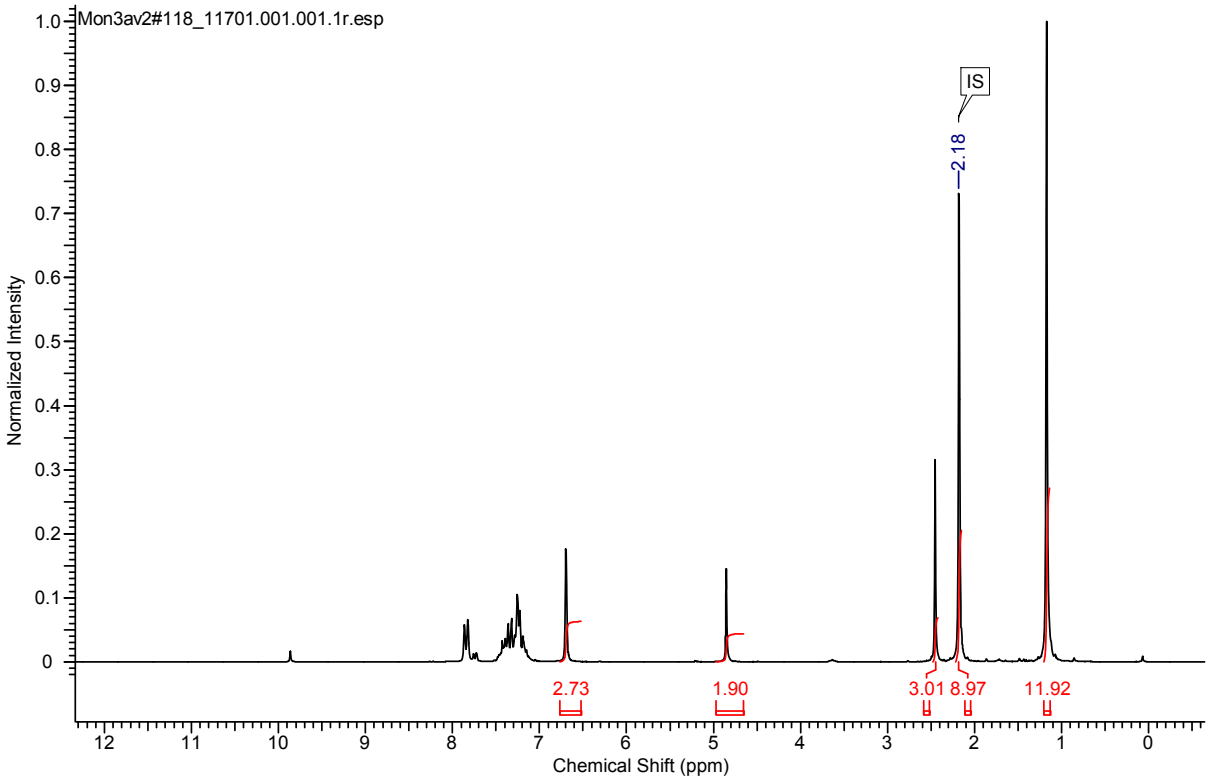


^{13}C NMR spectrum of **3m** ($CDCl_3$, 50.28 MHz, 298 K**)**

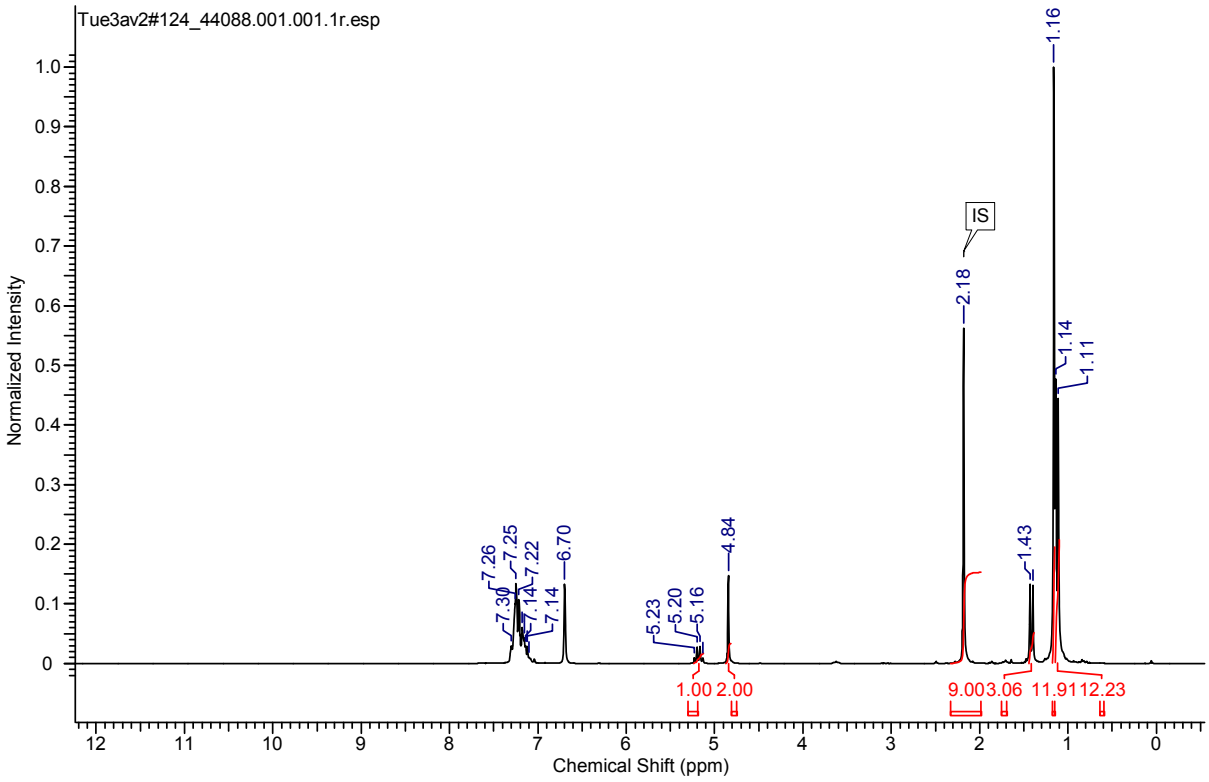


NMR spectra for competitive experiment for aldehyde/ketone hydroboration:

A. ^{1}H NMR for 1 Eq. PhCHO + 1 Eq. $PhCOCH_3$ + 1 Eq. HBpin + Catalyst

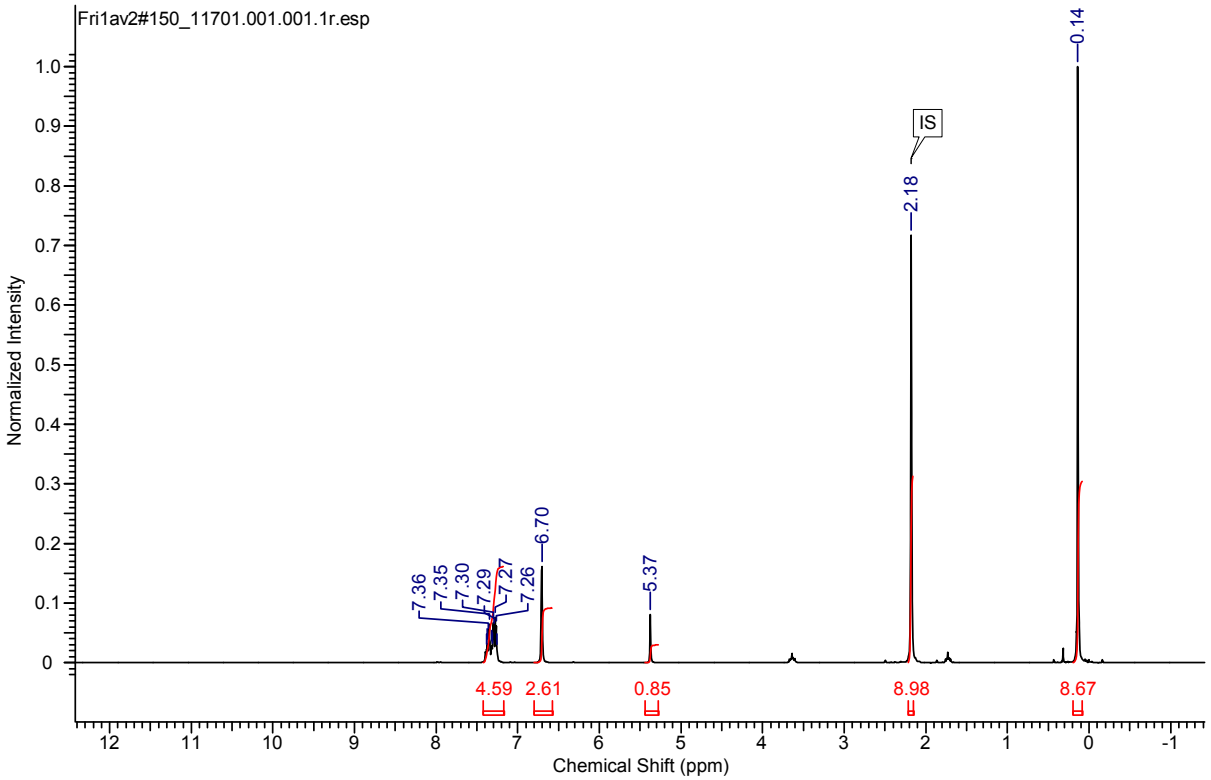


B. ^{1}H NMR for 1 Eq. PhCHO + 1 Eq. $PhCOCH_3$ + 2 Eq. HBpin + Catalyst

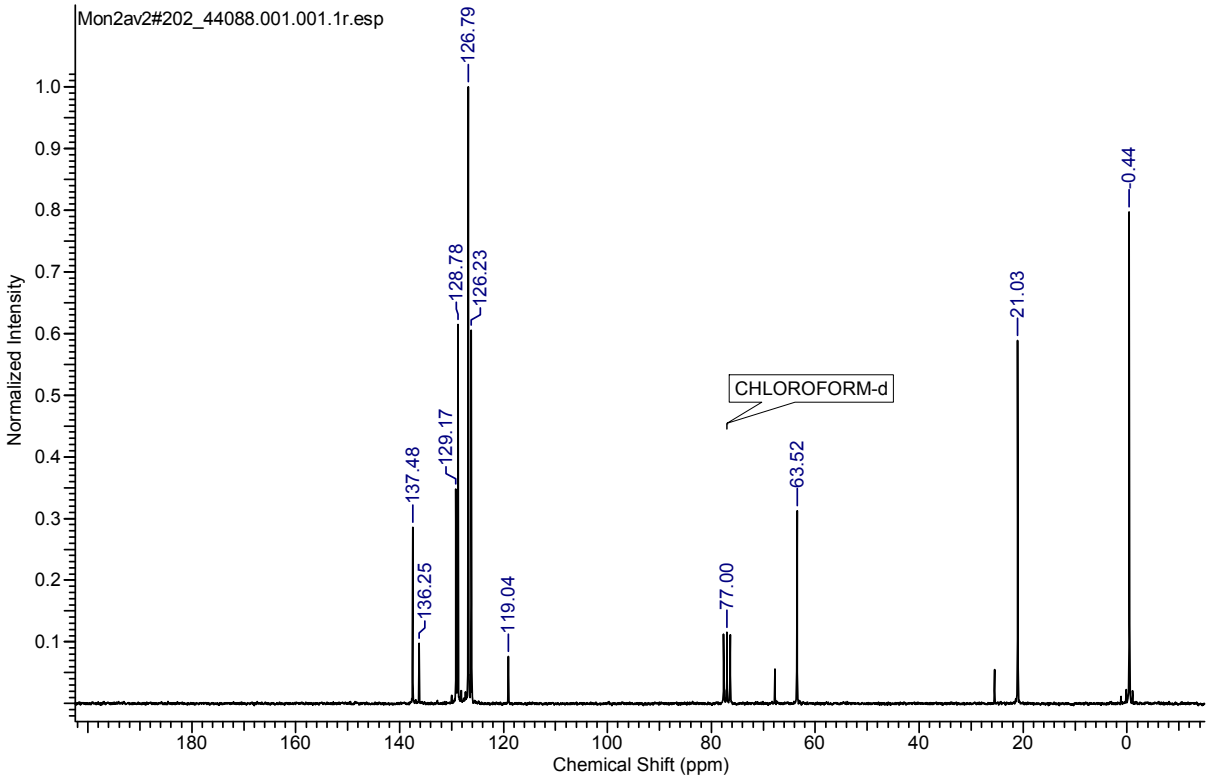


Representative NMR spectra for cyanosilylation:

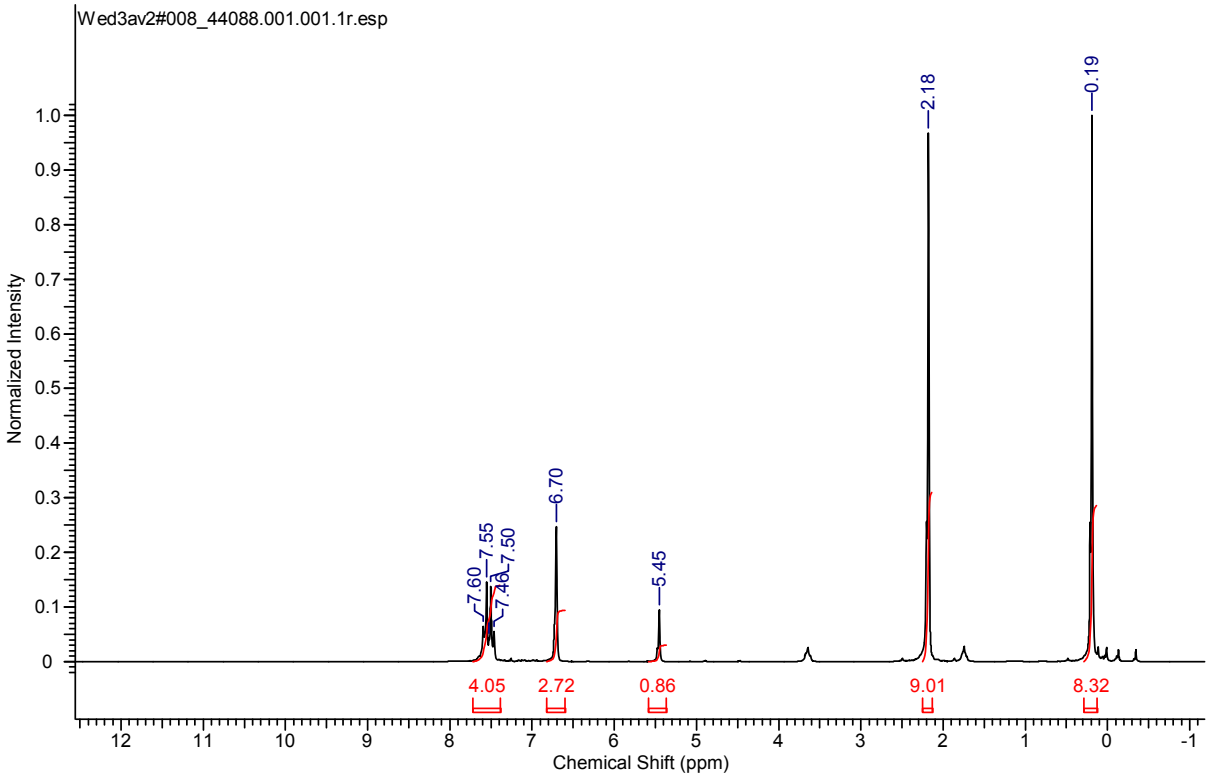
^{1}H NMR Spectrum of **4a** ($CDCl_3$, 200 MHz, 298 K)



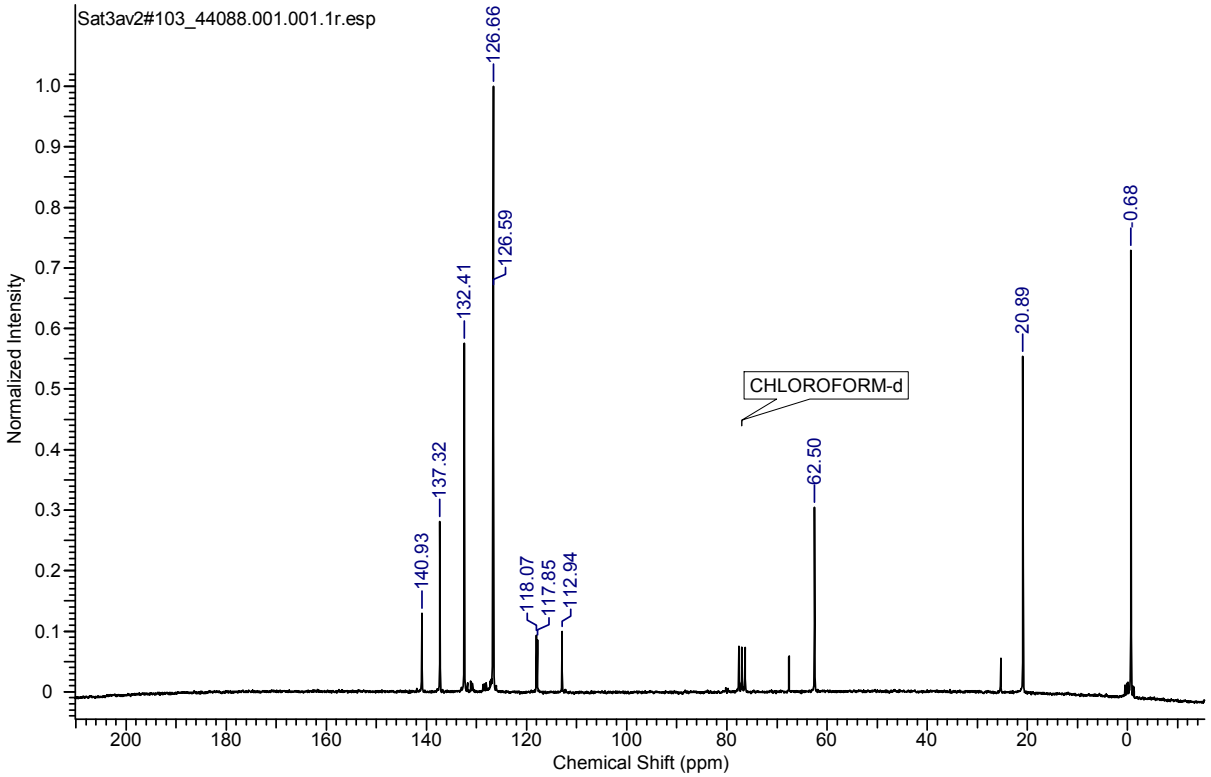
^{13}C NMR spectrum of **4a** ($CDCl_3$, 50.28 MHz, 298 K)



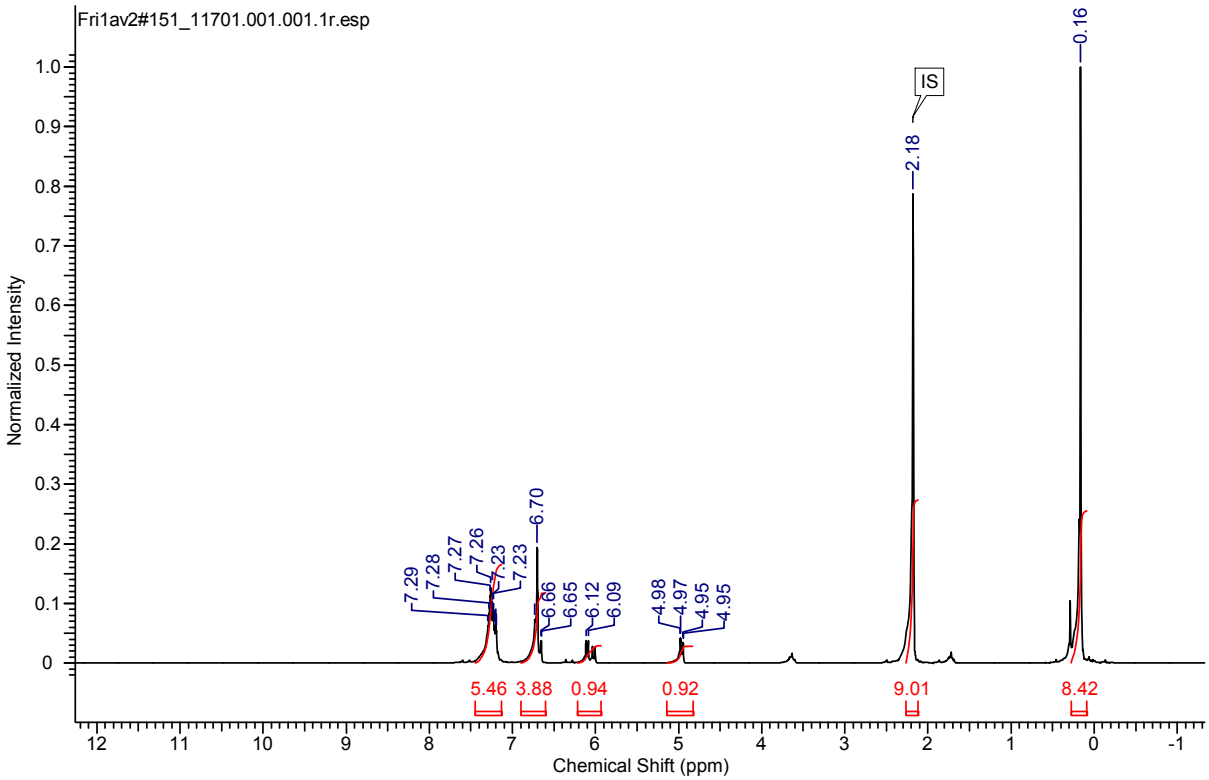
^{1}H NMR Spectrum of **4b** ($CDCl_3$, 200 MHz, 298 K)



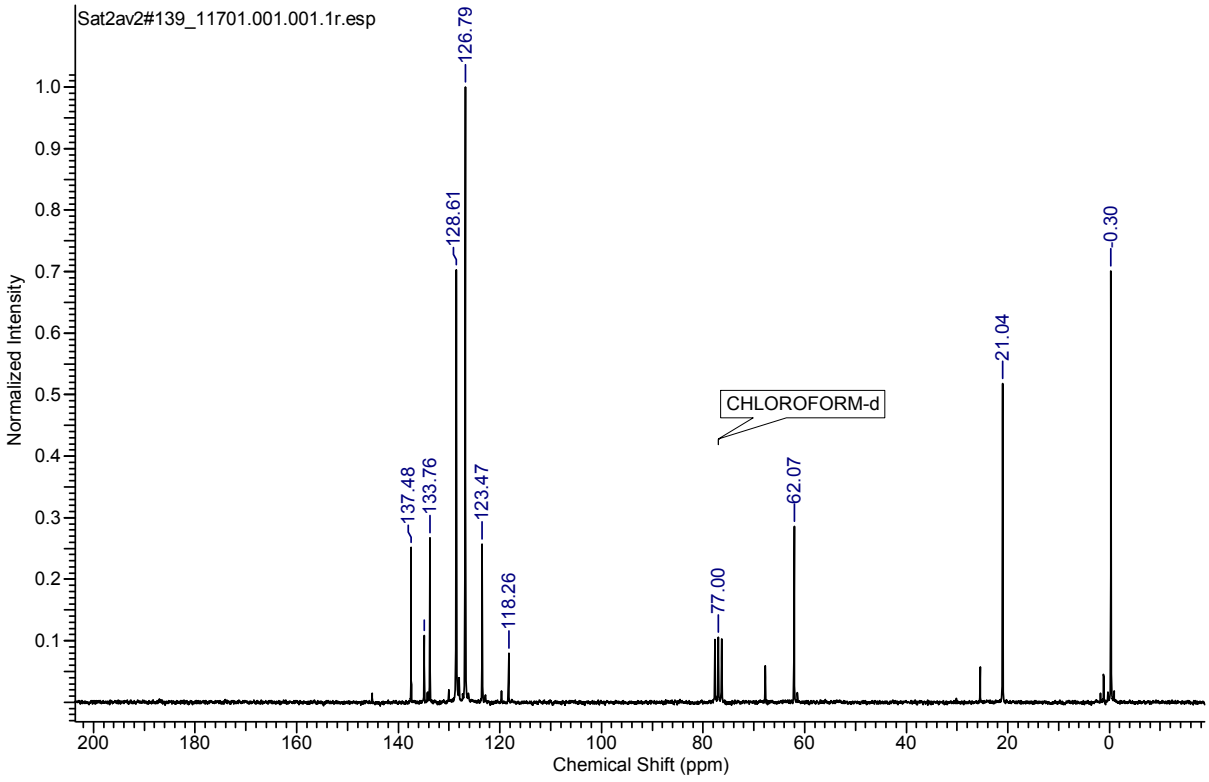
^{13}C NMR spectrum of **4b** ($CDCl_3$, 50.28 MHz, 298 K)



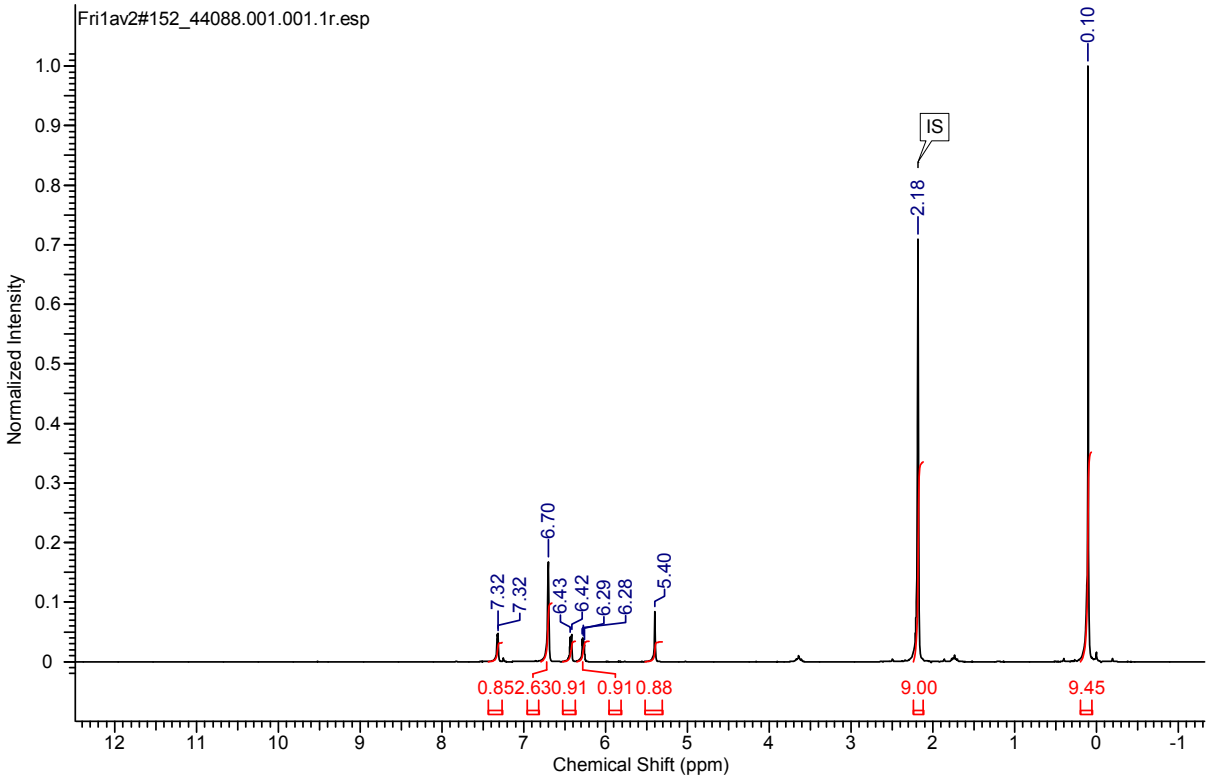
^{1}H NMR Spectrum of **4c** ($CDCl_3$, 200 MHz, 298 K)



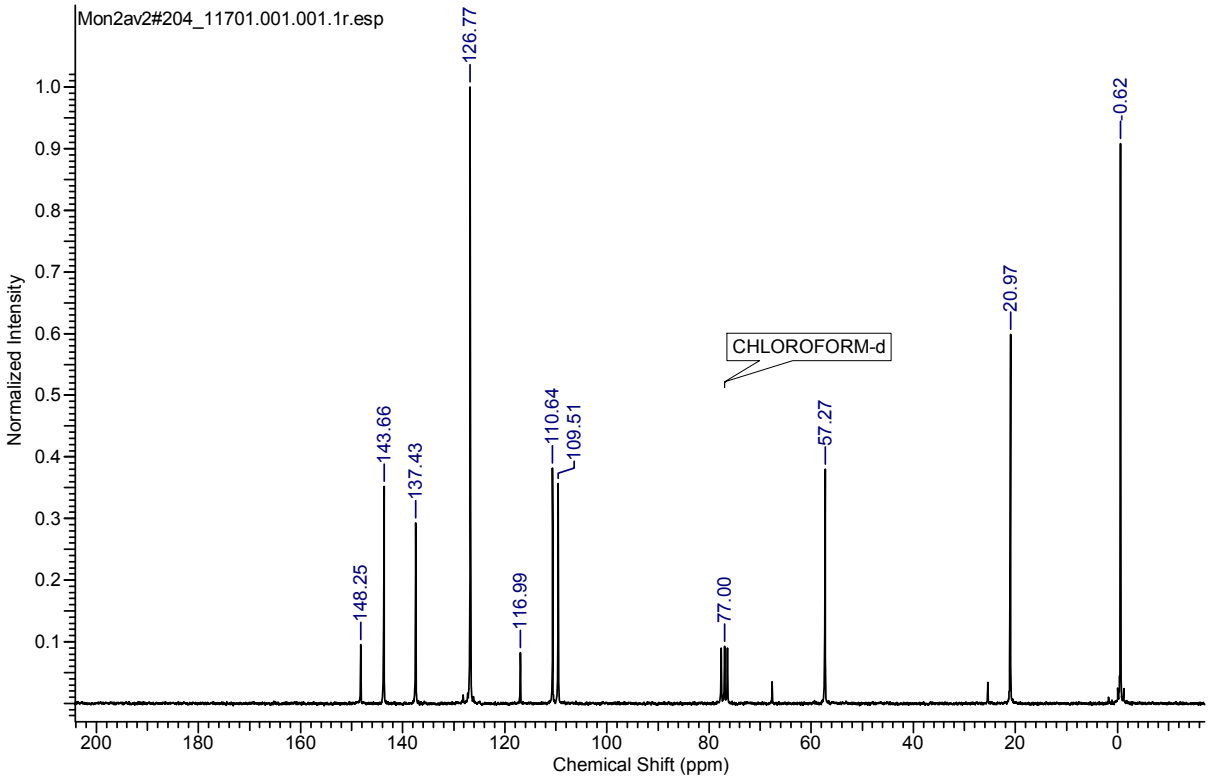
^{13}C NMR spectrum of **4c** ($CDCl_3$, 50.28 MHz, 298 K)



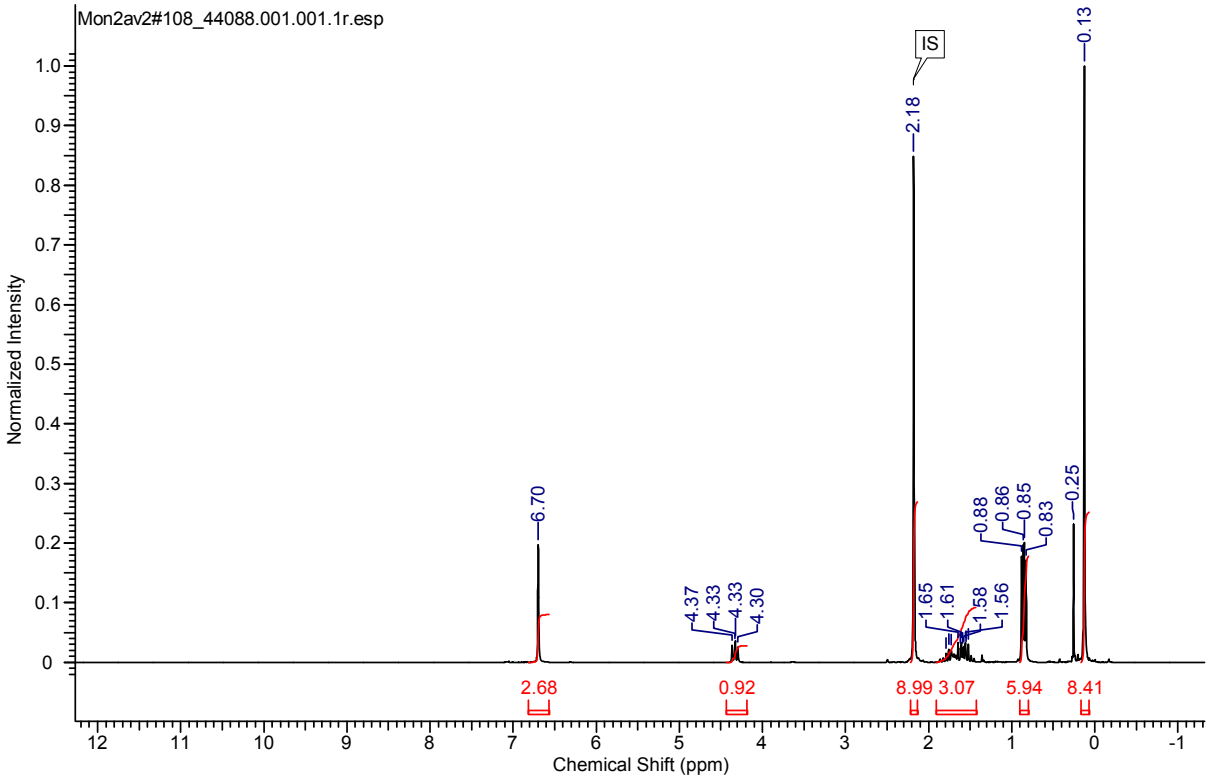
^{1}H NMR Spectrum of **4d** ($CDCl_3$, 200 MHz, 298 K)



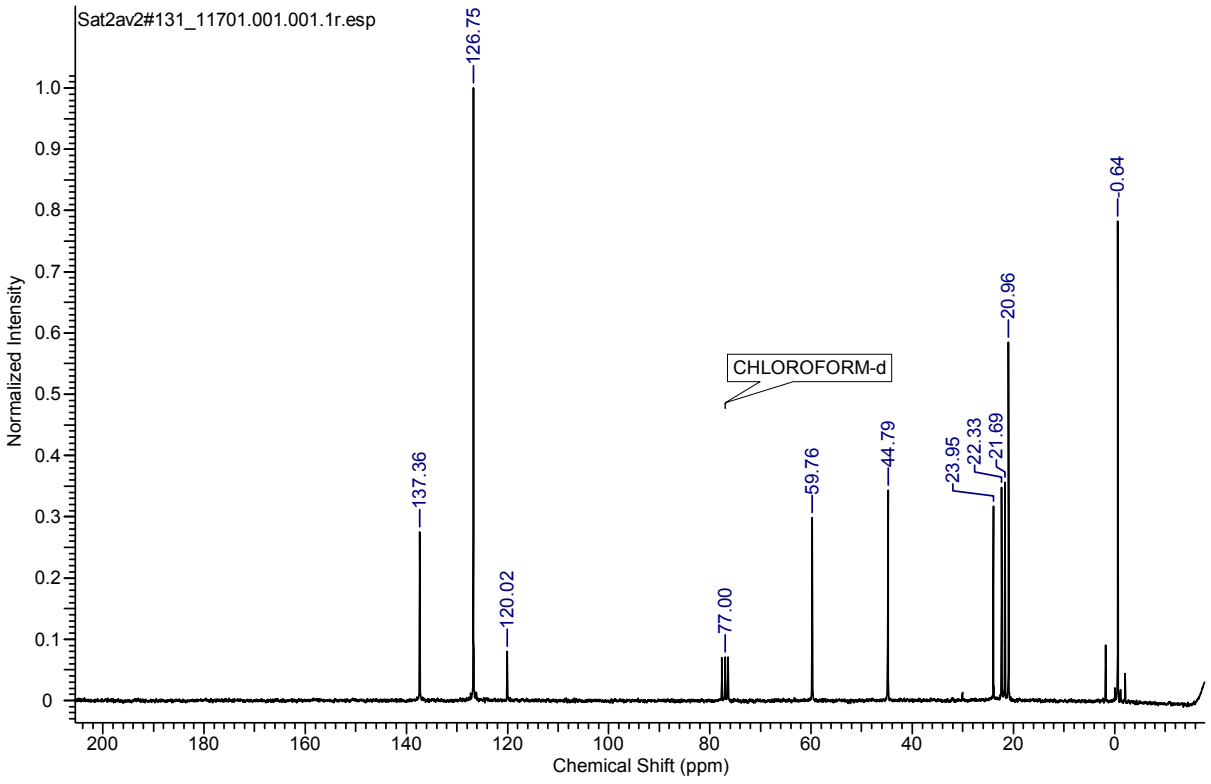
^{13}C NMR spectrum of **4d** ($CDCl_3$, 50.28 MHz, 298 K)



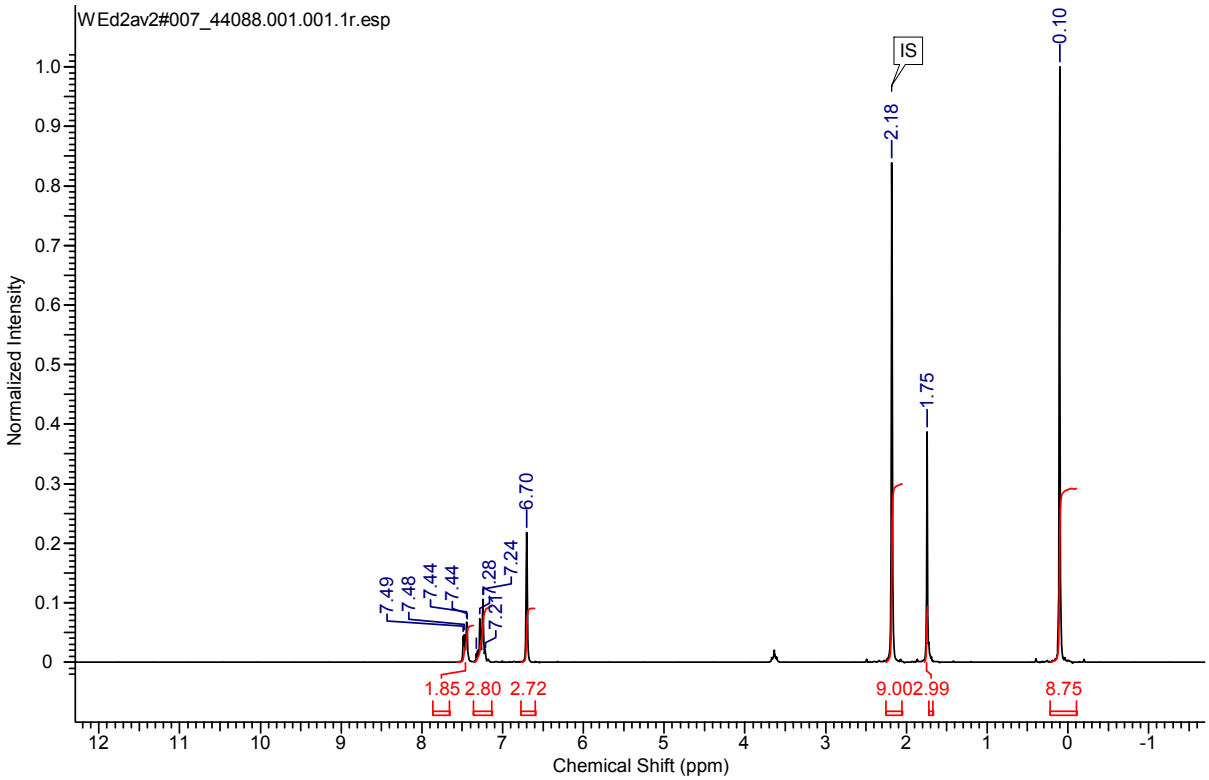
^{1}H NMR Spectrum of **4e** ($CDCl_3$, 200 MHz, 298 K)



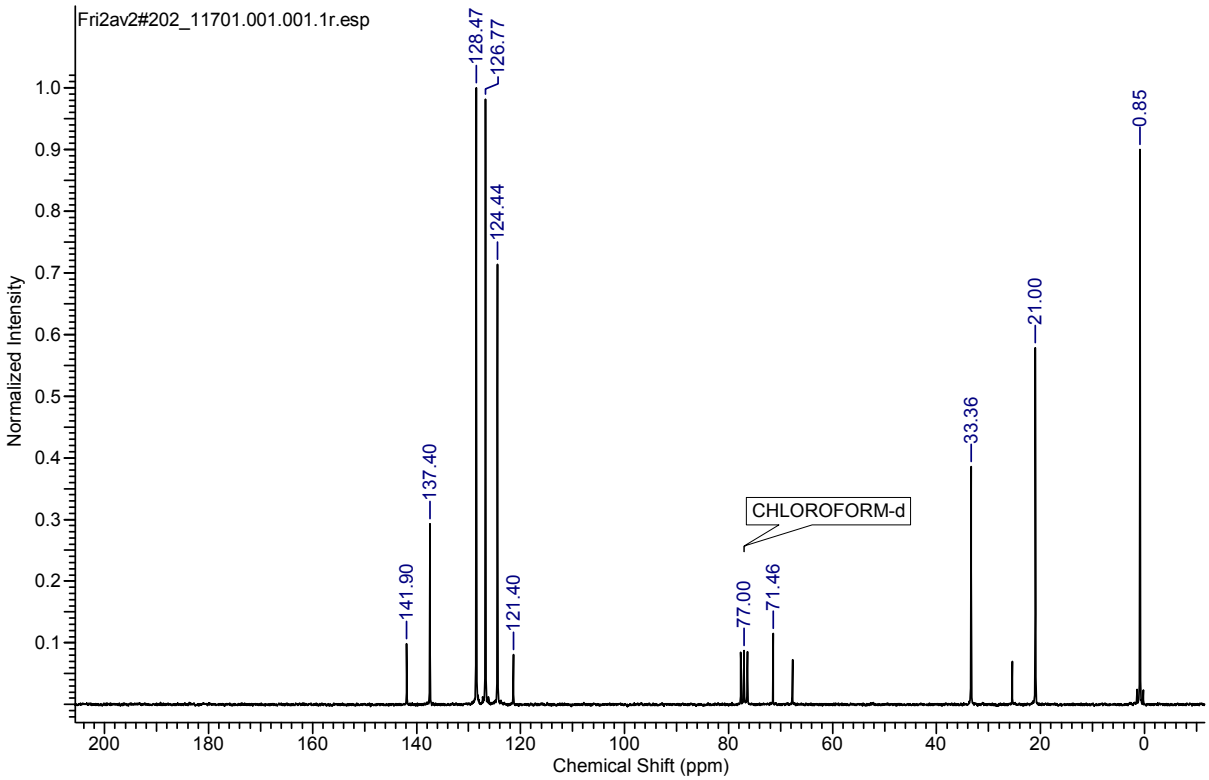
^{13}C NMR spectrum of **4e** ($CDCl_3$, 50.28 MHz, 298 K)



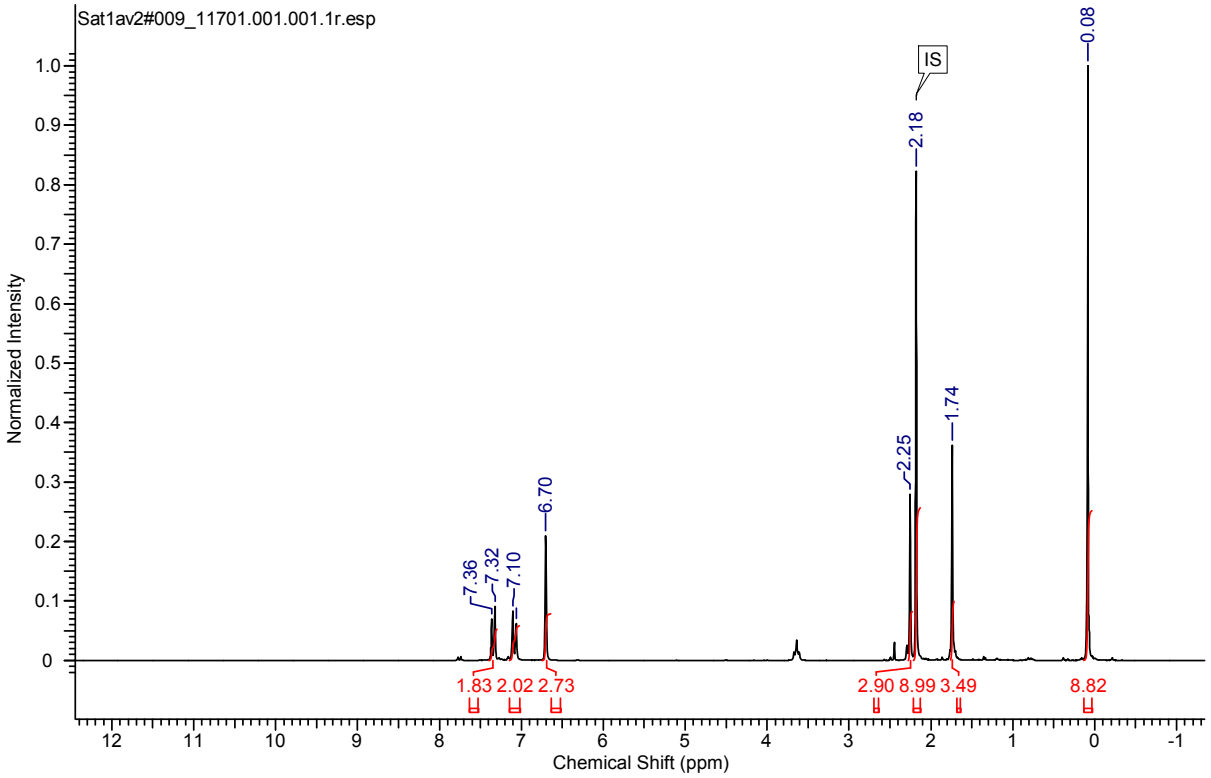
^{1}H NMR Spectrum of **4f** ($CDCl_3$, 200 MHz, 298 K)



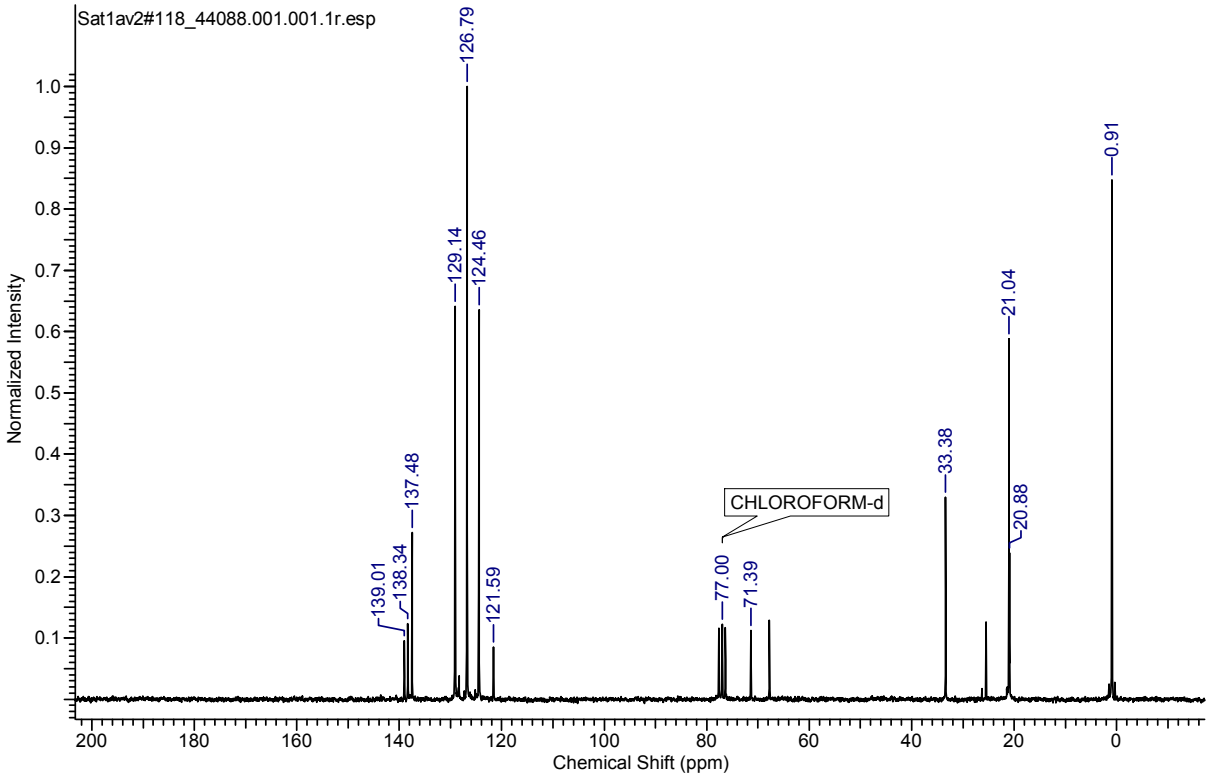
^{13}C NMR spectrum of **4f** ($CDCl_3$, 50.28 MHz, 298 K)



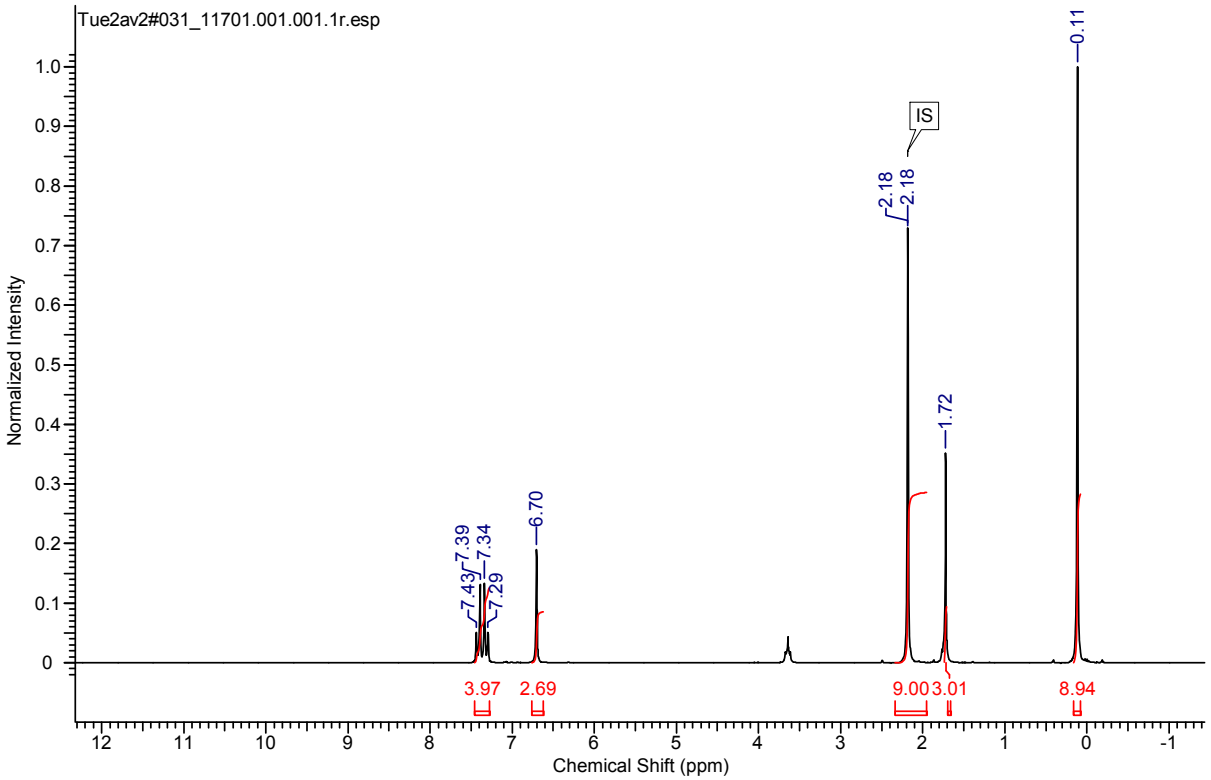
^{1}H NMR Spectrum of **4g** ($CDCl_3$, 200 MHz, 298 K)



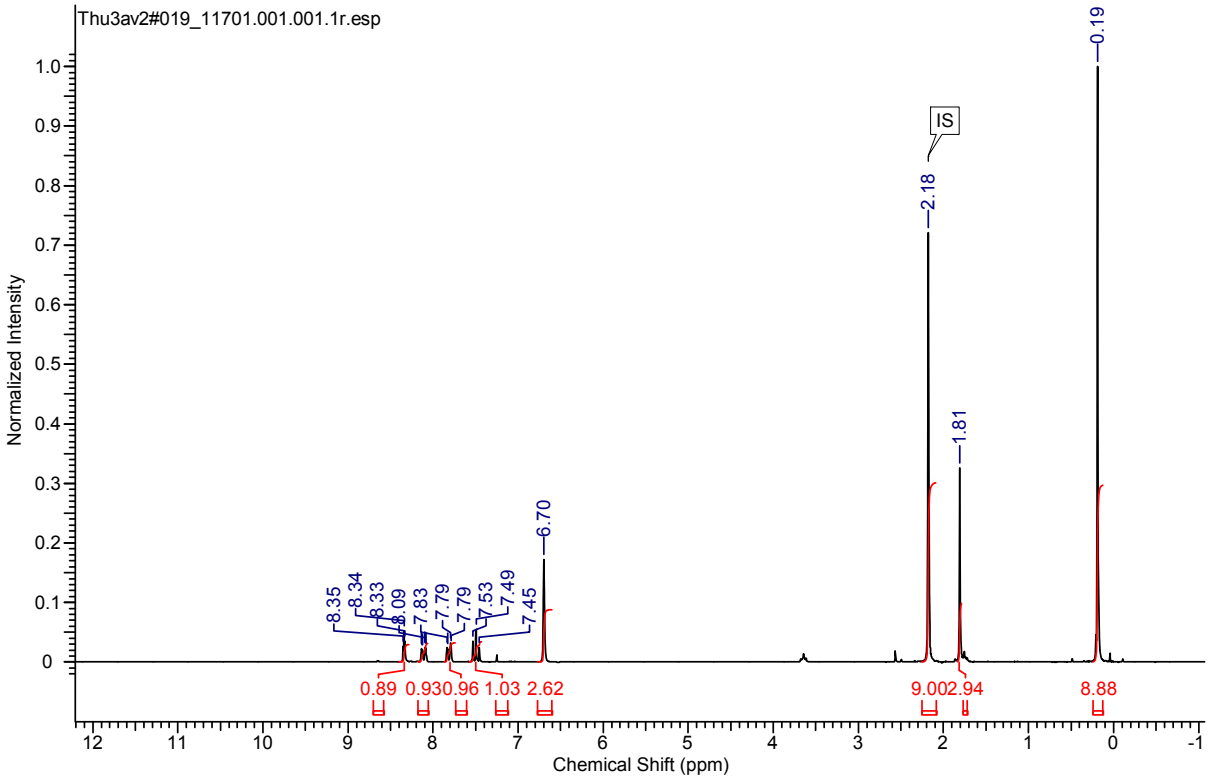
^{13}C NMR spectrum of **4g** ($CDCl_3$, 50.28 MHz, 298 K)



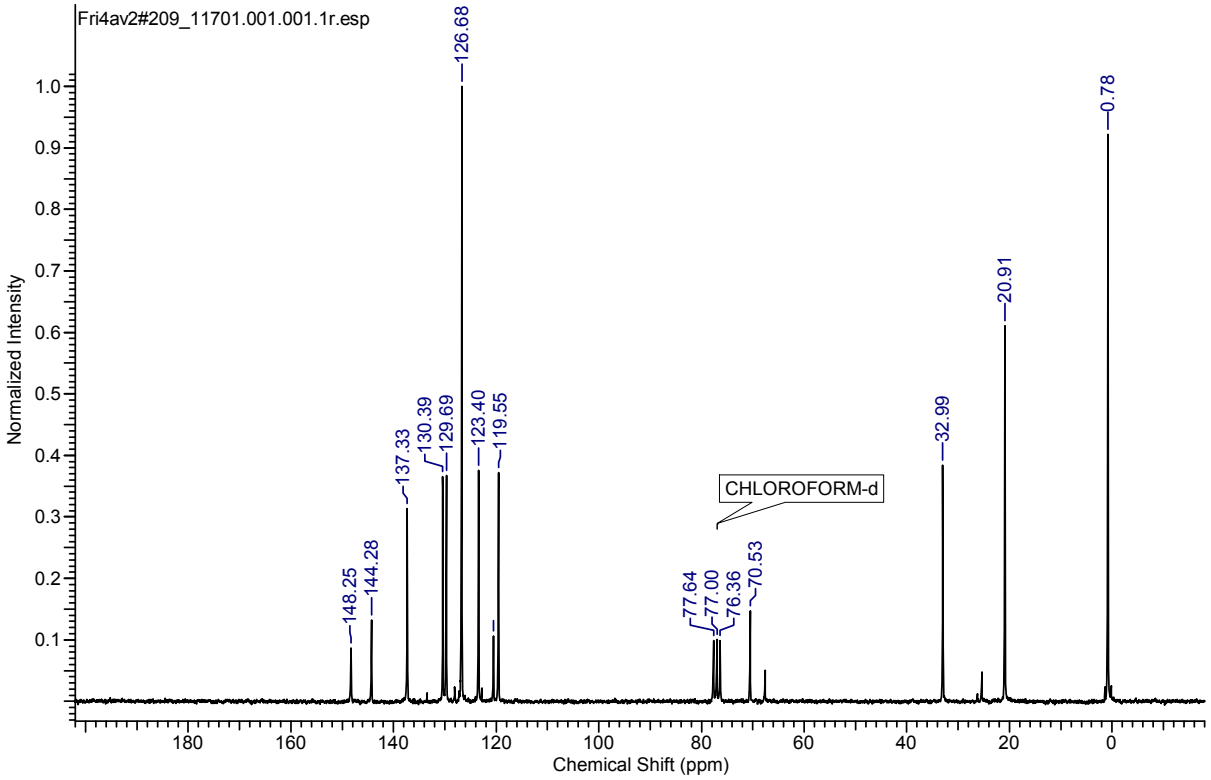
^{1}H NMR Spectrum of **4h** ($CDCl_3$, 200 MHz, 298 K)



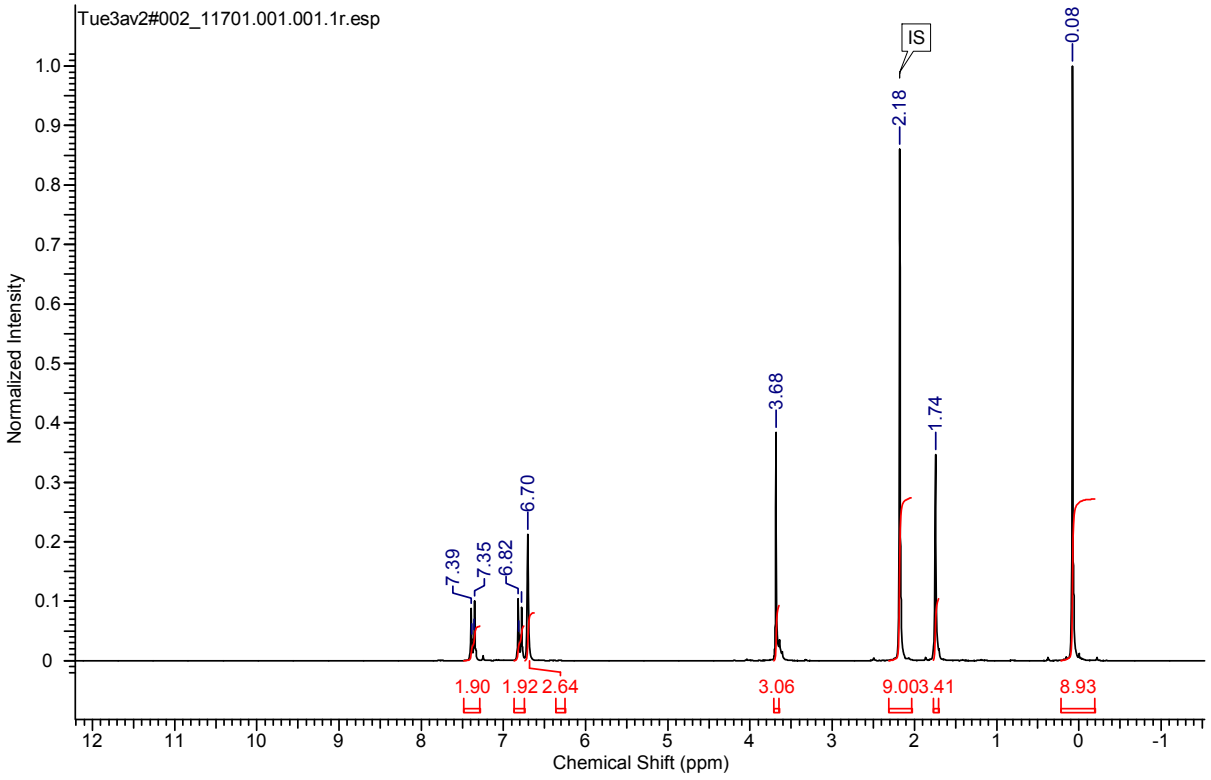
^{1}H NMR Spectrum of **4i** ($CDCl_3$, 200 MHz, 298 K)



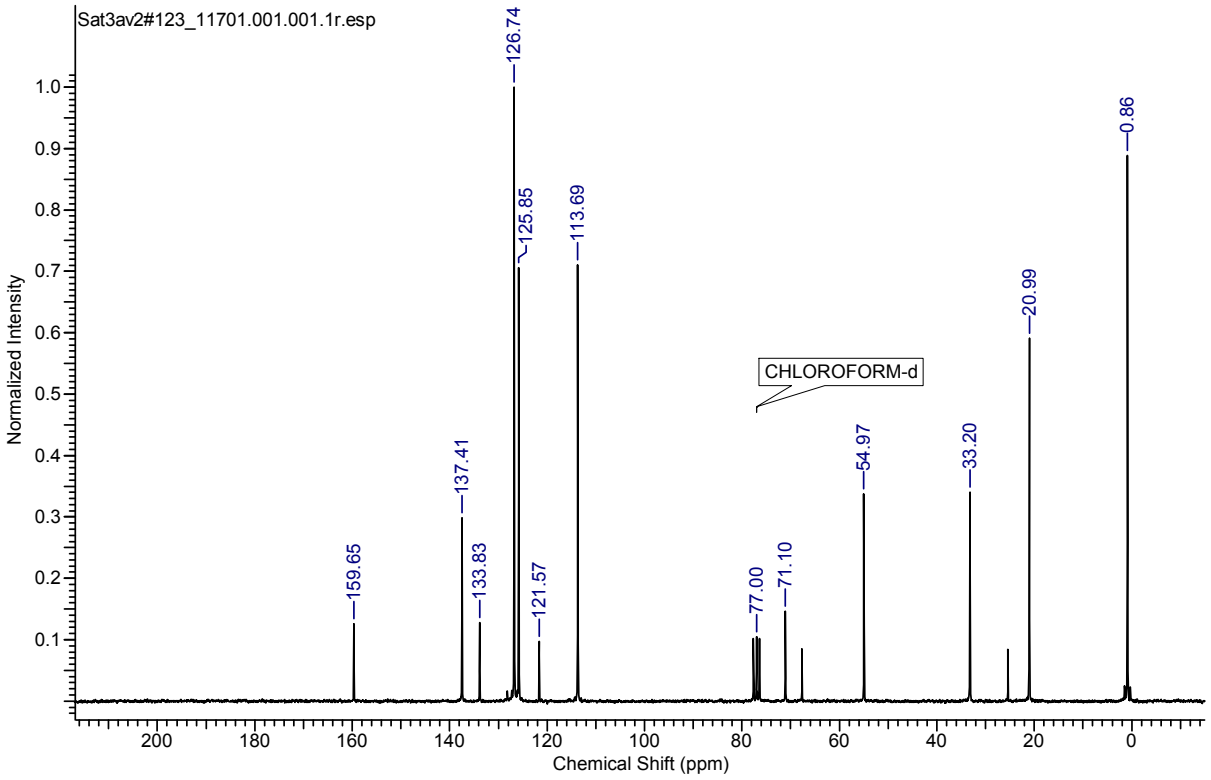
^{13}C NMR spectrum of **4i** ($CDCl_3$, 50.28 MHz, 298 K)



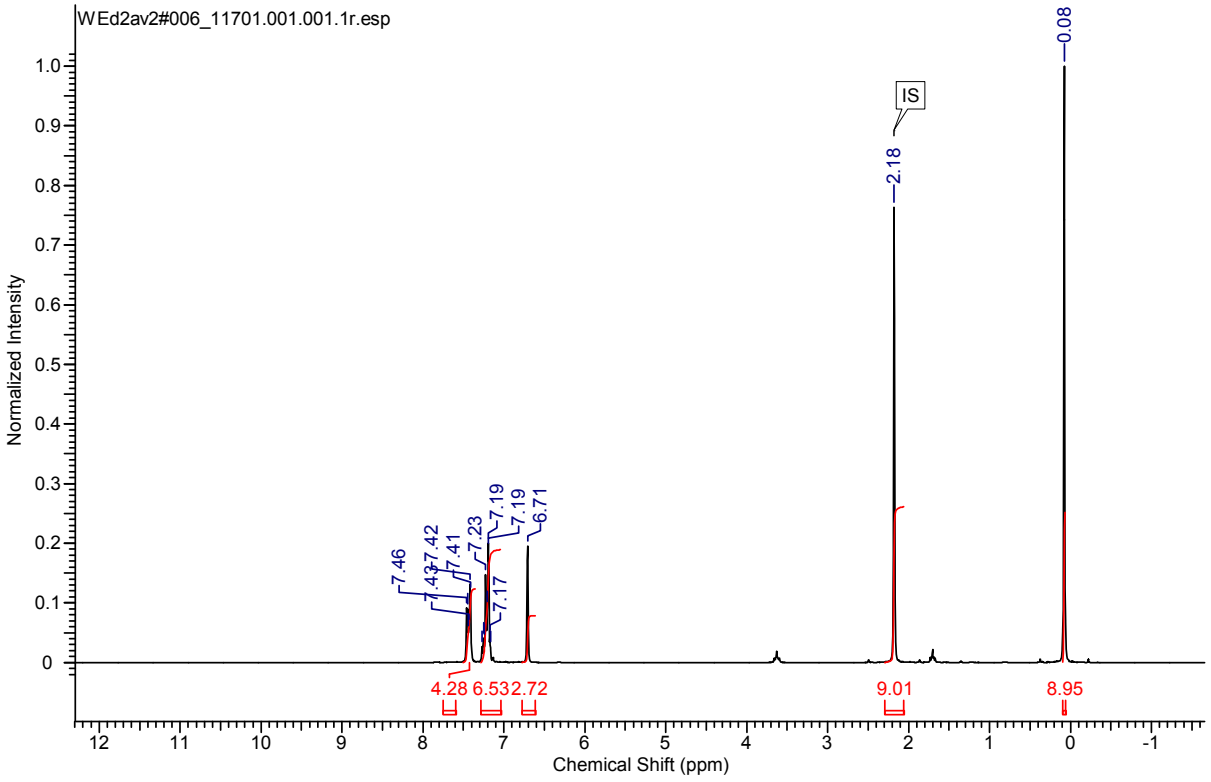
^{1}H NMR Spectrum of **4j** ($CDCl_3$, 200 MHz, 298 K)



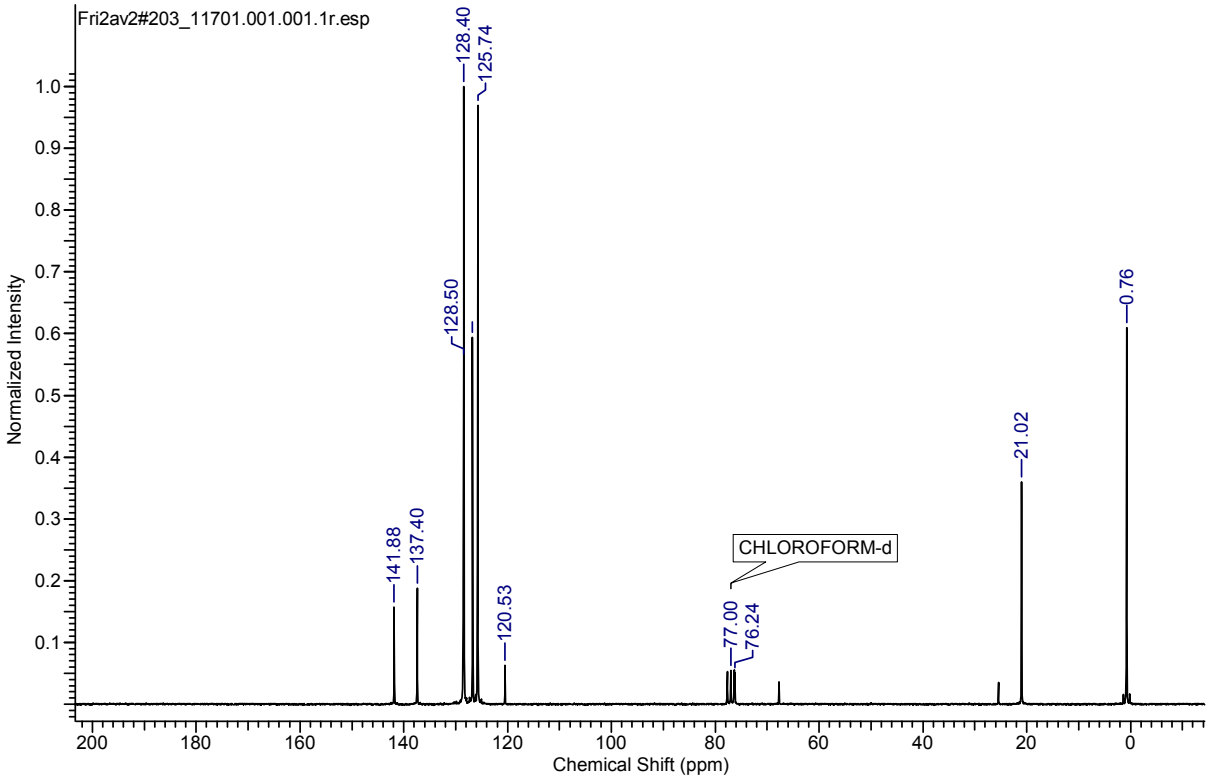
^{13}C NMR spectrum of **4j** ($CDCl_3$, 50.28 MHz, 298 K)



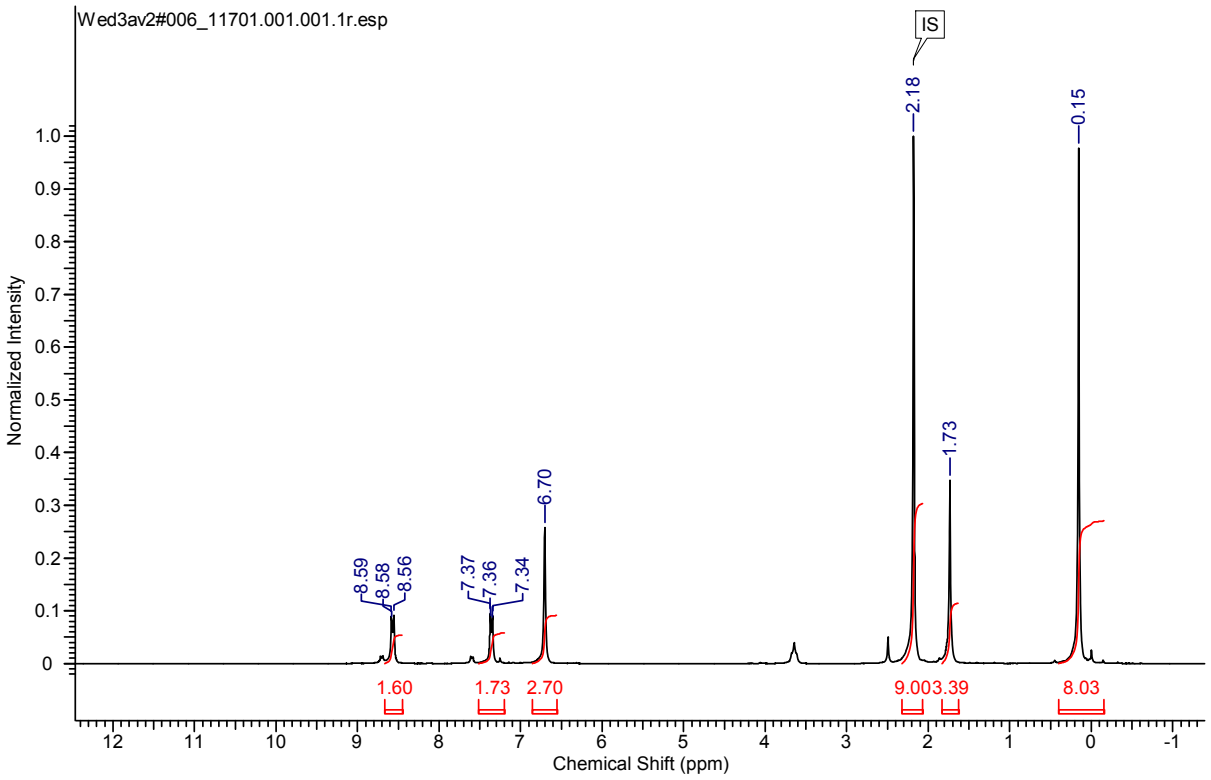
^{1}H NMR Spectrum of **4k** ($CDCl_3$, 200 MHz, 298 K)



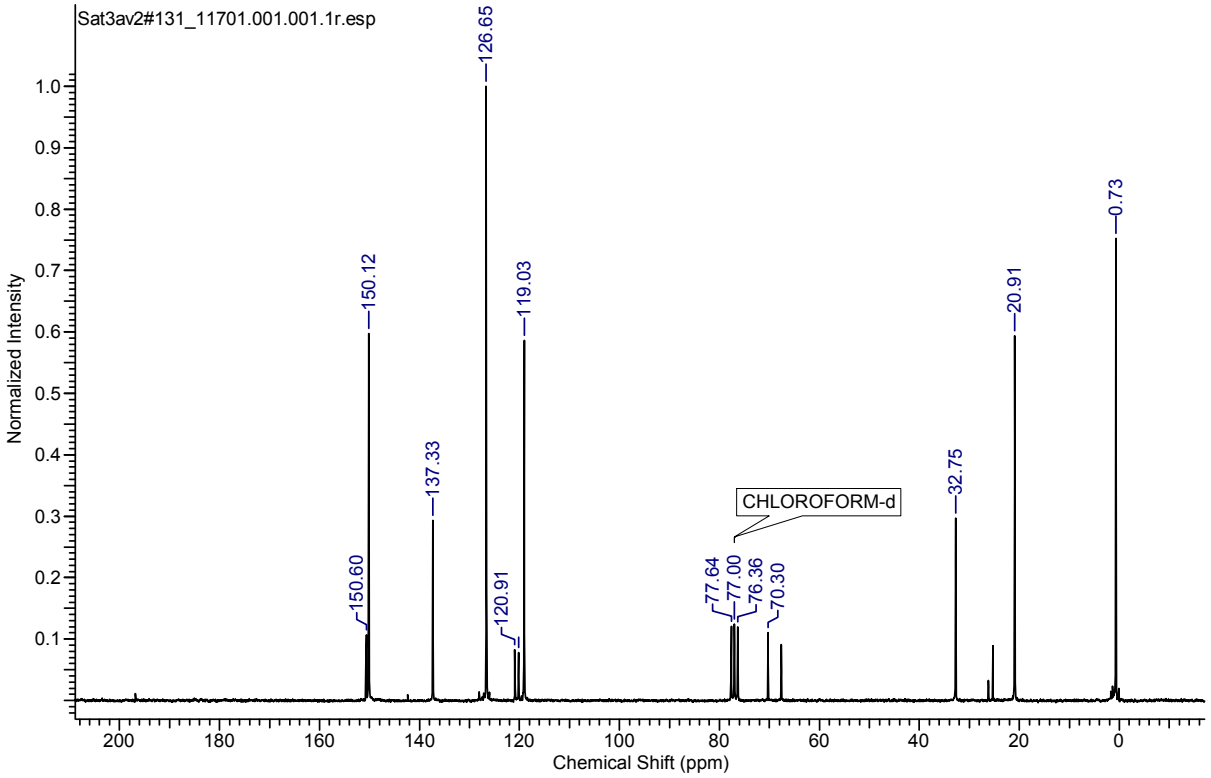
^{13}C NMR spectrum of **4k** ($CDCl_3$, 50.28 MHz, 298 K)



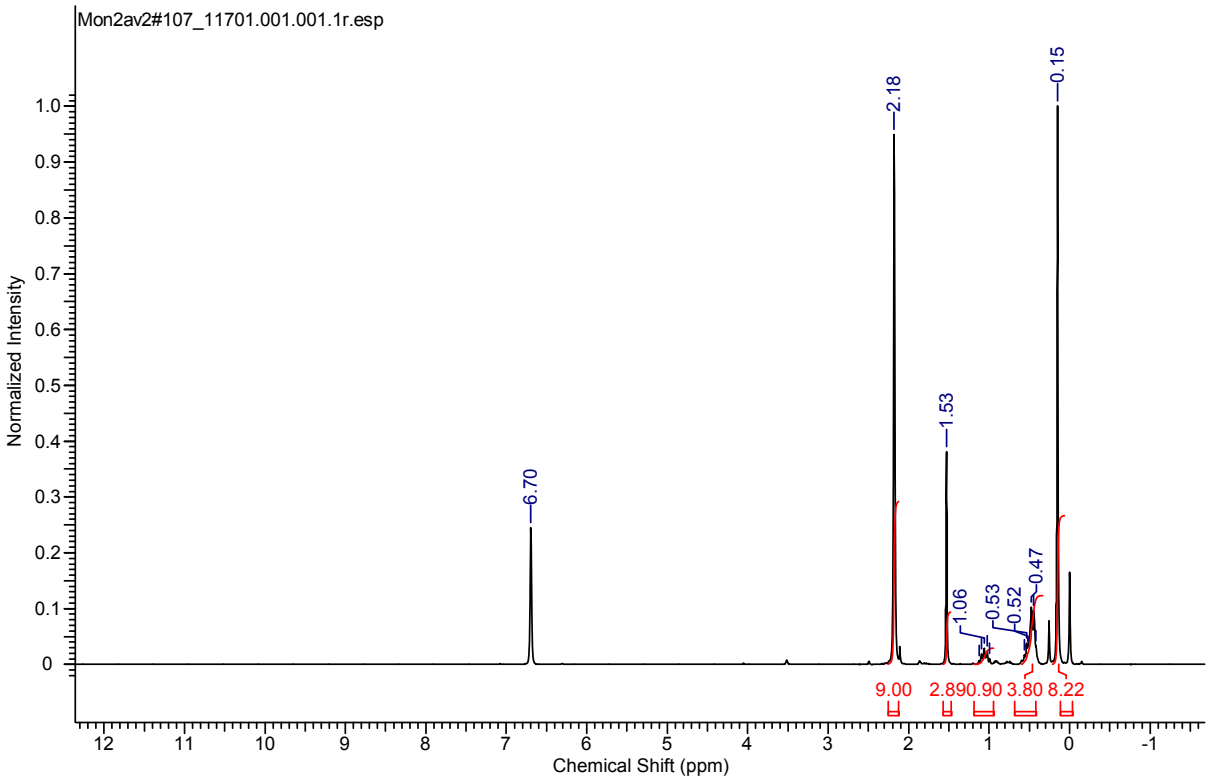
^{1}H NMR Spectrum of **4l** ($CDCl_3$, 200 MHz, 298 K)



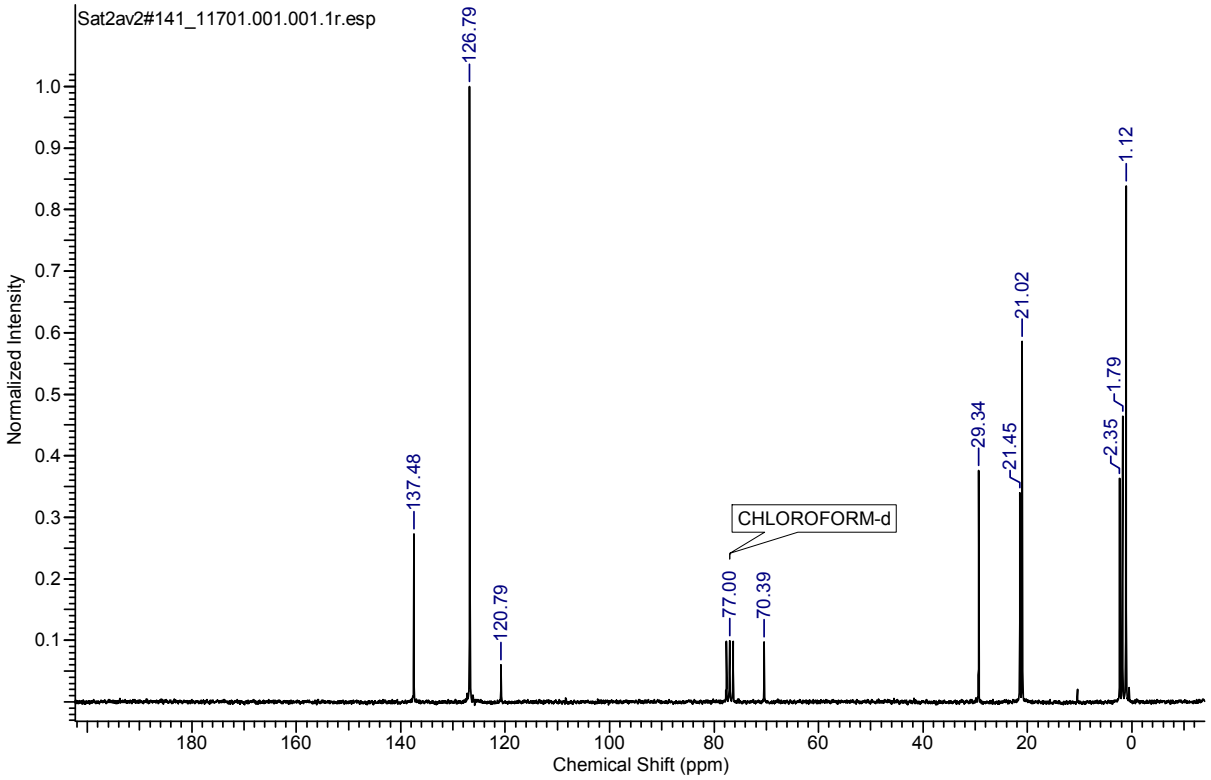
^{13}C NMR spectrum of **4l** ($CDCl_3$, 50.28 MHz, 298 K)



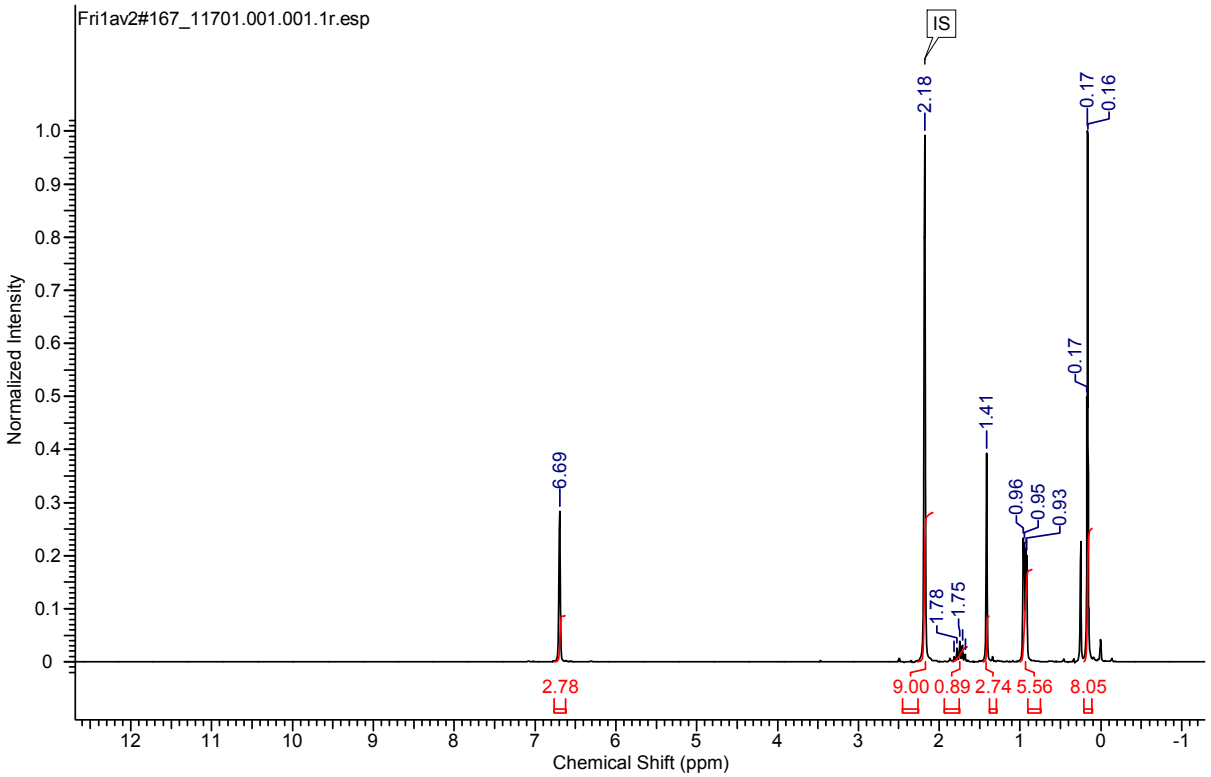
^{1}H NMR Spectrum of **4m** ($CDCl_3$, 200 MHz, 298 K)



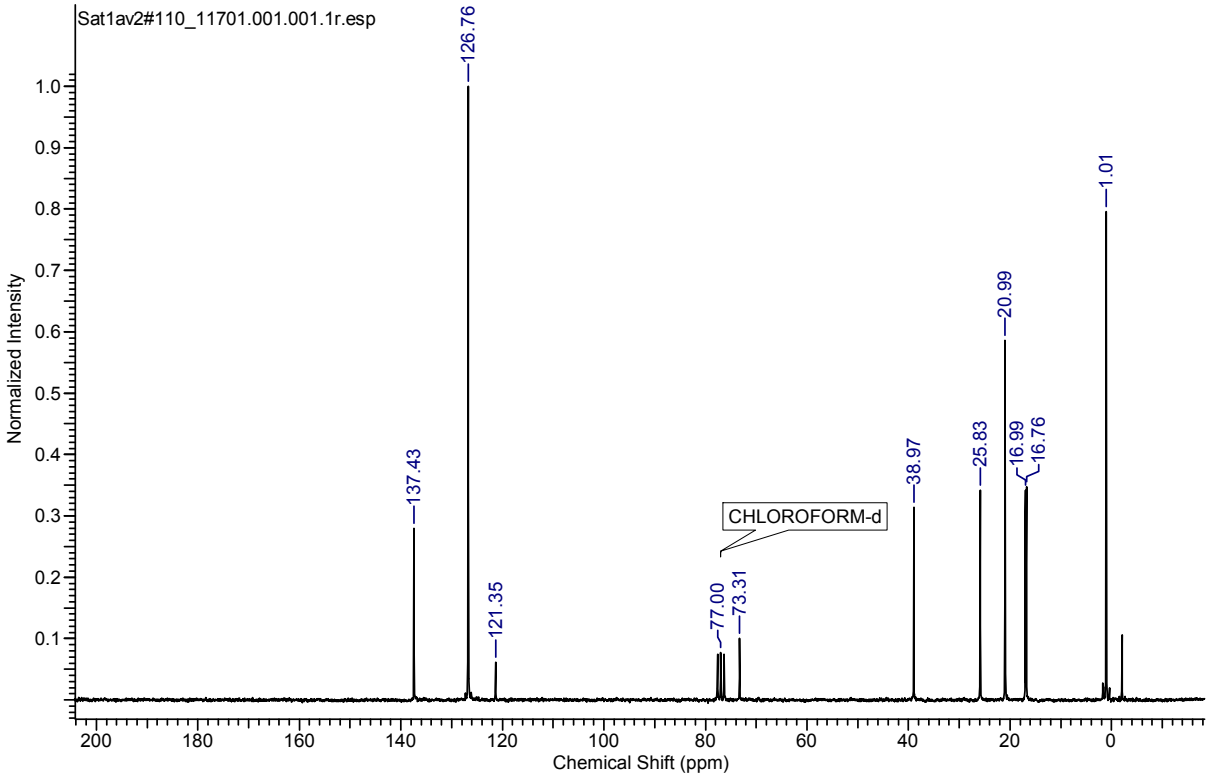
^{13}C NMR spectrum of **4m** ($CDCl_3$, 50.28 MHz, 298 K)



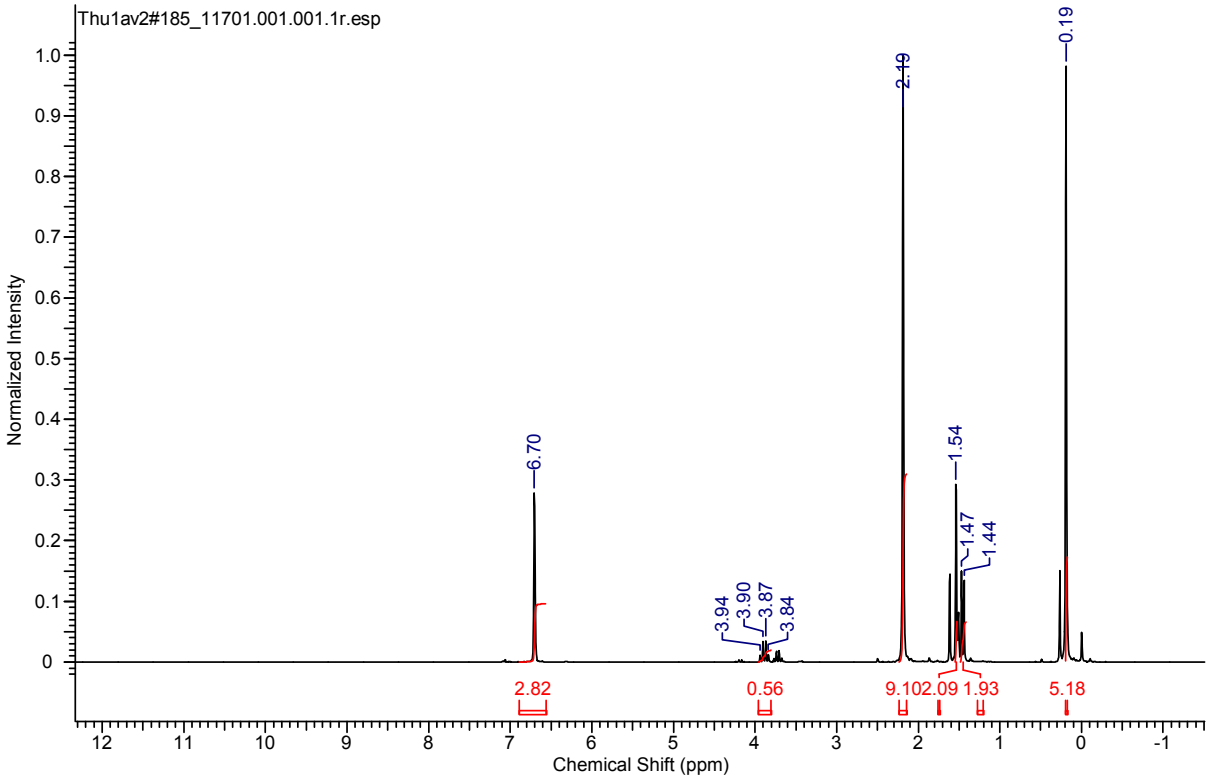
^{1}H NMR Spectrum of **4n** ($CDCl_3$, 200 MHz, 298 K)



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



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

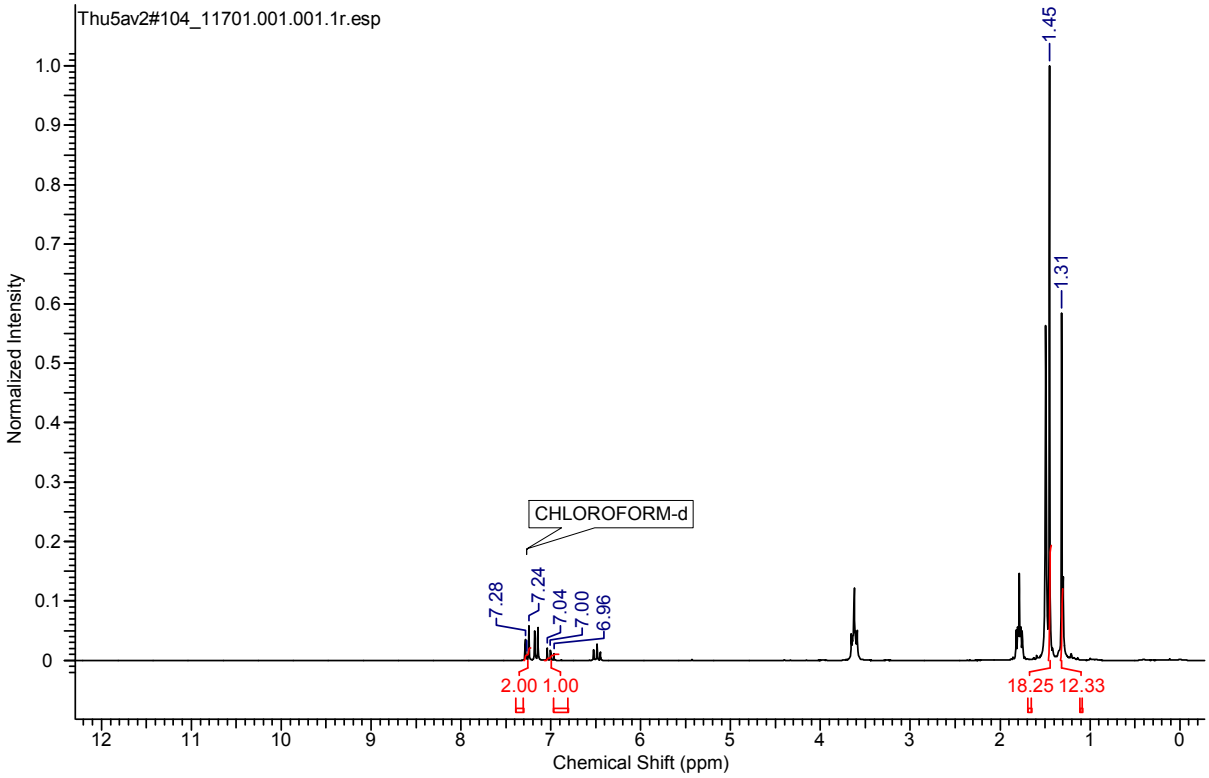


Stoichiometric reaction of catalyst 1a and HBpin:

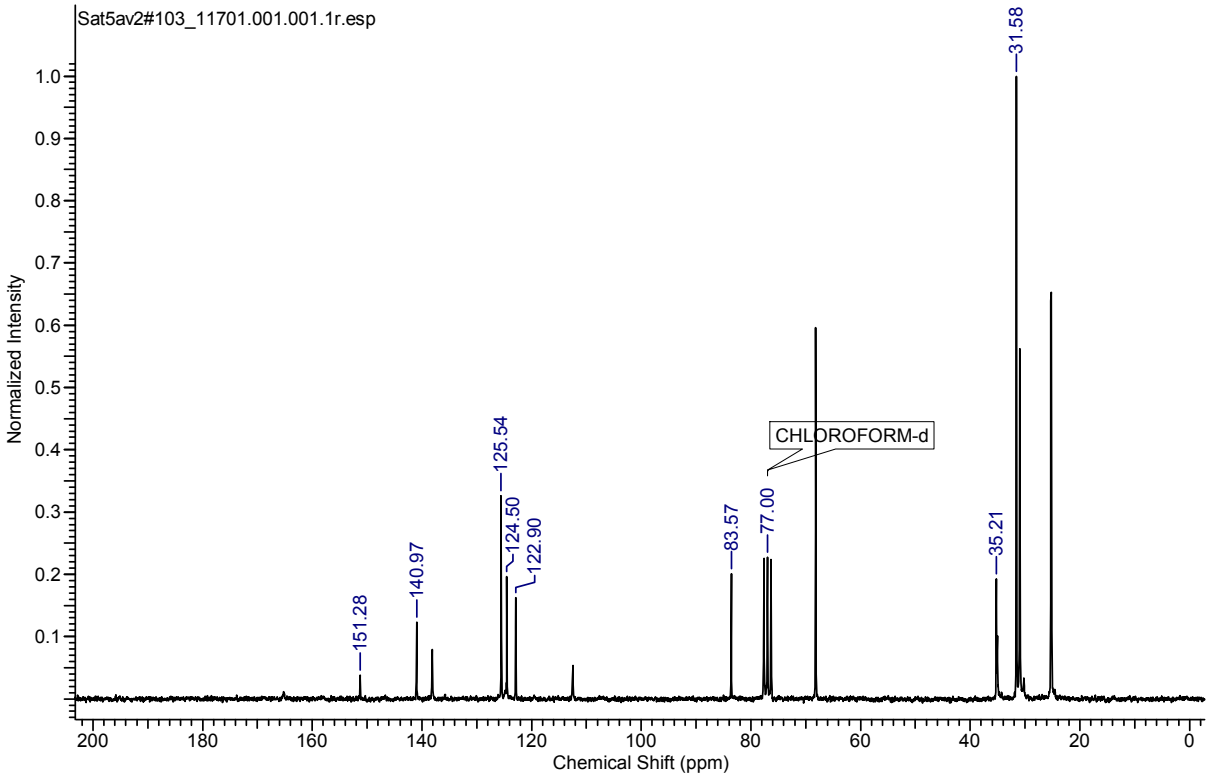
A solution of HBpin (0.09 g, 0.70 mmol) in THF (2 mL) was added dropwise to the THF solution (8 mL) of **1a** (0.2 g, 0.70 mmol) at –78 °C. The reaction mixture was stirred at –78 °C for 15 min then at room temperature for overnight. After addition of HBpin, solution was clear upto 3-4 h and after that white ppt started forming slowly. The solution was filtered and then filtrate was dried for charateriztion. Yield **(**0.207 g, 88.8%**)**, ^{1}H NMR ($CDCl_3$, 200 MHz, 298 K): δ 7.26 (d, $^{3}J_{H\text{-}H}$= 7.58 Hz, 2H, Ar*H*), 7.00 (t, 1H, Ar*H*), 1.45 (s, 18H, C(C*H*$_3$)$_3$), 1.31 (s, 12H, C(C*H*$_3$)$_2$) ppm; ^{13}C{1H} NMR ($CDCl_3$, 50.28MHz, 298 K): δ 151.28 (*Ph*), 140.97 (*Ph*), 125.54 (*Ph*), 122.90 (*Ph*), 83.57 (*C*(CH$_3$)$_2$), 35.21 (C(*C*H$_3$)$_2$), 31.58 (C(*C*H$_3$)$_2$) ppm; ^{11}B NMR (toluene-*d*$_8$, 128 MHz, 298 K): δ 21.62, 4.66, -39.83 (quintet) ppm.

Representative NMR spectra for Stoichiometric reaction of catalyst 1a and HBpin:

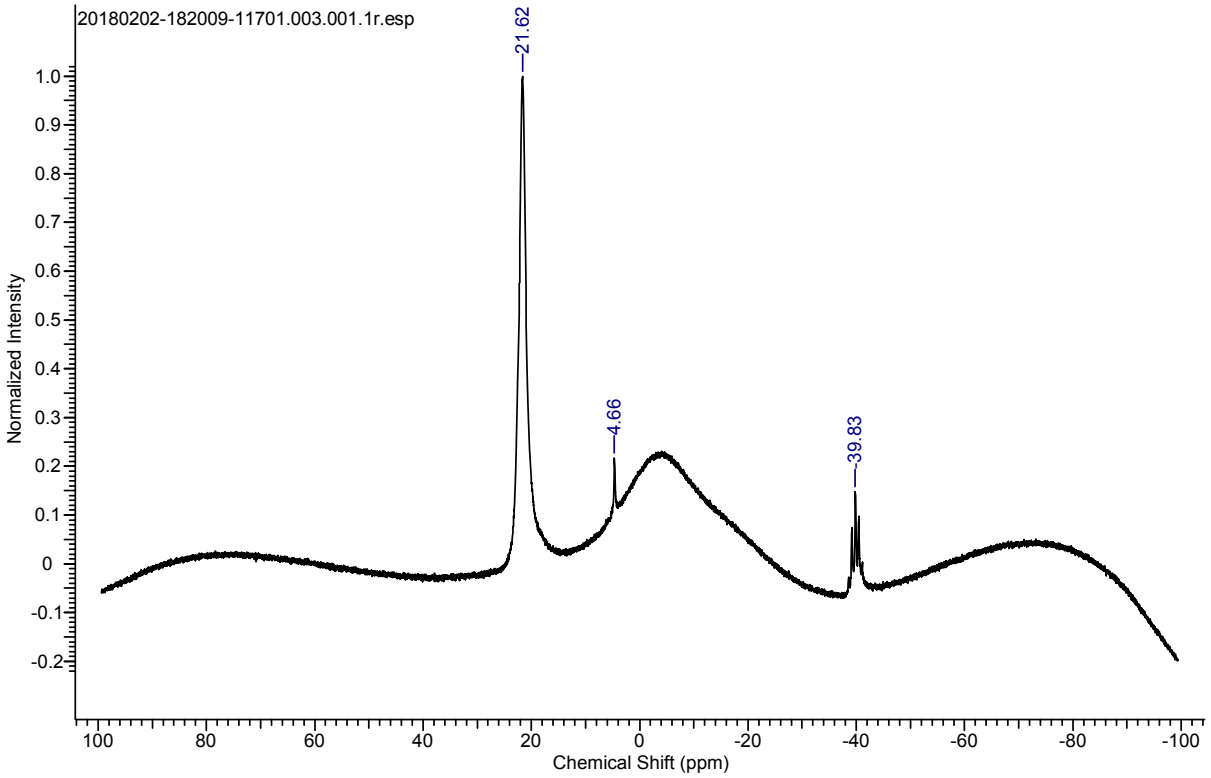
^{1}H NMR spectrum for 1:1 reaction of **1a** and HBpin ($CDCl_3$, 200 MHz, 298 K)



^{13}C NMR spectrum for 1:1 reaction of **1a** and HBpin ($CDCl_3$, 50.28 MHz, 298 K)

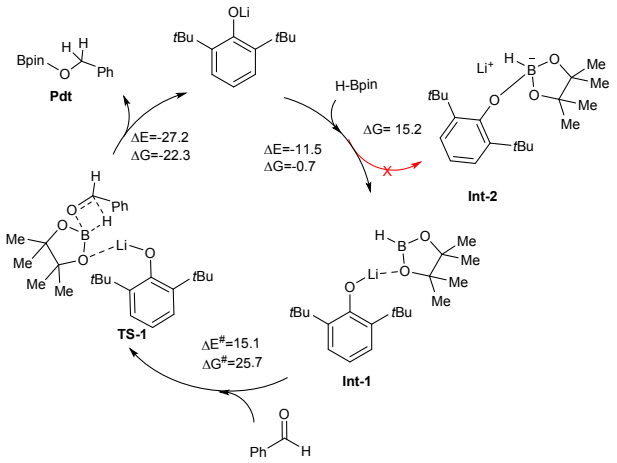


^{11}B NMR spectrum for 1:1 reaction of **1a** and HBpin (toluene-d_8, 128 MHz, 298 K)



Details of DFT calculations:

All the calculations in this study have been performed with density functional theory (DFT), with the aid of the Turbomole 7.1 suite of programs,[S4] using the PBE functional. [S5] The TZVP[S6] basis set has been employed. The resolution of identity (RI),[S7] along with the multipole accelerated resolution of identity (marij)[S8] approximations have been employed for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. Solvent correction were incorporated with optimization calculations using the COSMO model,[S9] with tetrahydrofuran (ε = 7.58) 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.



Scheme S2. The catalytic cycle and reaction mechanism for the aldehyde hydroboration by catalyst **1a**, 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

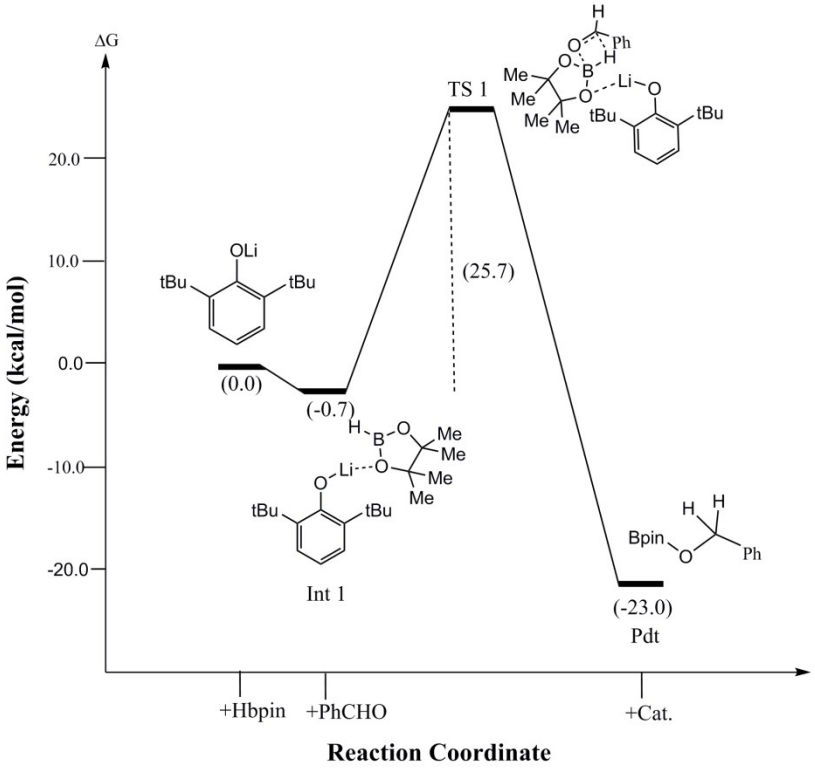


Figure S1. Thereaction energy profile diagram for the catalytic aldehyde hydroboration by catalyst **1a**. The values (in kcal/mol) have been calculated at the PBE/TZVP level of theory with DFT.

NBO analysis

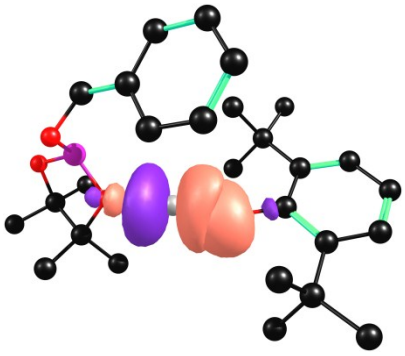
For investigating the bonding interaction in **TS-1** of **Scheme 4** we have done natural bond orbitals (NBO) analysis procedures as implemented in the Gaussian 09 programme. The analyses was performed at the PBEPBE/TZVP optimized geometry using the PBE density functional together with the all electron TZVP basis set.

In order to gain insight into the interaction of the alkoxide Oxygen with the Li, the intermolecular charge transfer in the complex has been analysed with the natural bond orbital (NBO) analysis. The energetic estimate of donor (i) – acceptor (j) orbital interactions can be obtained by the second order perturbation theory analysis of the Fock matrix in the NBO basis. The donor–acceptor interaction energy E(2) is given by

$$E(2) = \Delta E(i,j) = q(i,j)F(i,j)^2/\{\varepsilon(i) - \varepsilon(j)\}$$

where q(i) is the donor orbital occupancy, ε(i) and ε(j) are the diagonal elements (orbital energies), and F(i,j) is the off-diagonal NBO Fock matrix element. In the present investigation, the important interactions between the alkoxide Oxygen and the Li have been analysed.

To see the bonding interaction between alkoxide oxygen with lithium and pinacolborane oxygen with lithium in **TS-1**, we have done the natural bond orbital analysis. From the NBO analysis we have found that there is a very strong interaction between alkoxide oxygen with Lithium (32.1 kcal/mol) compare to the relatively weak interaction between pinacolborane oxygen with Lithium (13.5 kcal/mol). These second order perturbation energies suggest that there is a covalent interaction between alkoxide oxygen with Lithium which support our proposed mechanistic pathway.



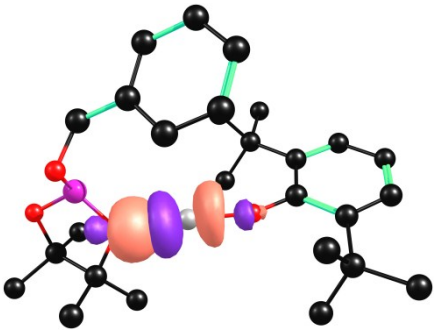
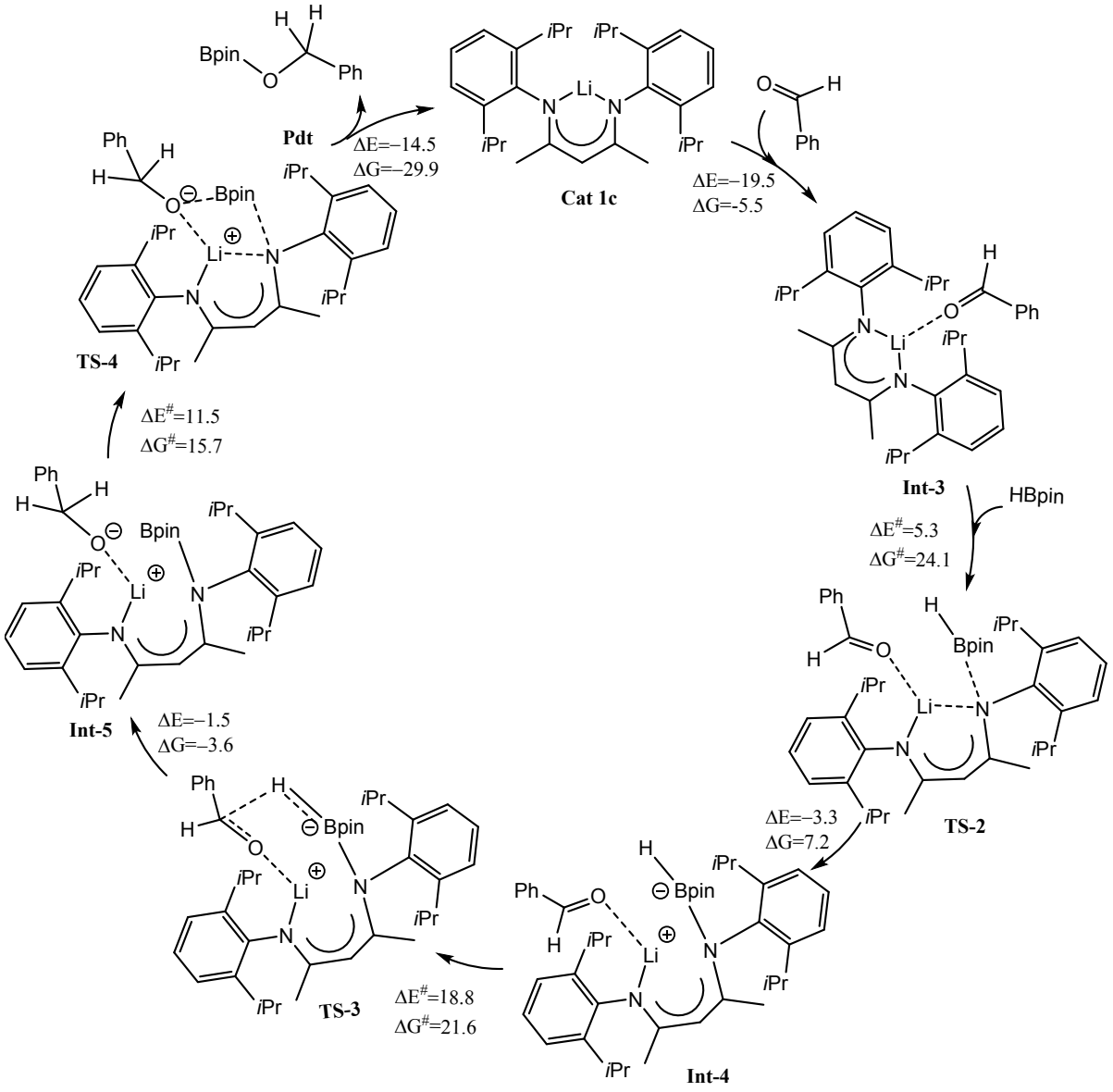


Figure S2a. Strong σ (LP (alkoxide O)→LP* (Li)) interactions and **Figure S2b**. Weak σ (LP (pinacolborane O)→ LP*(Li)) interaction



Scheme S3. The catalytic cycle and the reaction mechanism for the aldehyde hydroboration by catalyst **1c**, calculated at the PBE/TZVP level of theory with DFT. ΔG and $\Delta G^{\#}$ represent the free energy of the reaction and the free energy of activation respectively. All values are in kcal/mol.

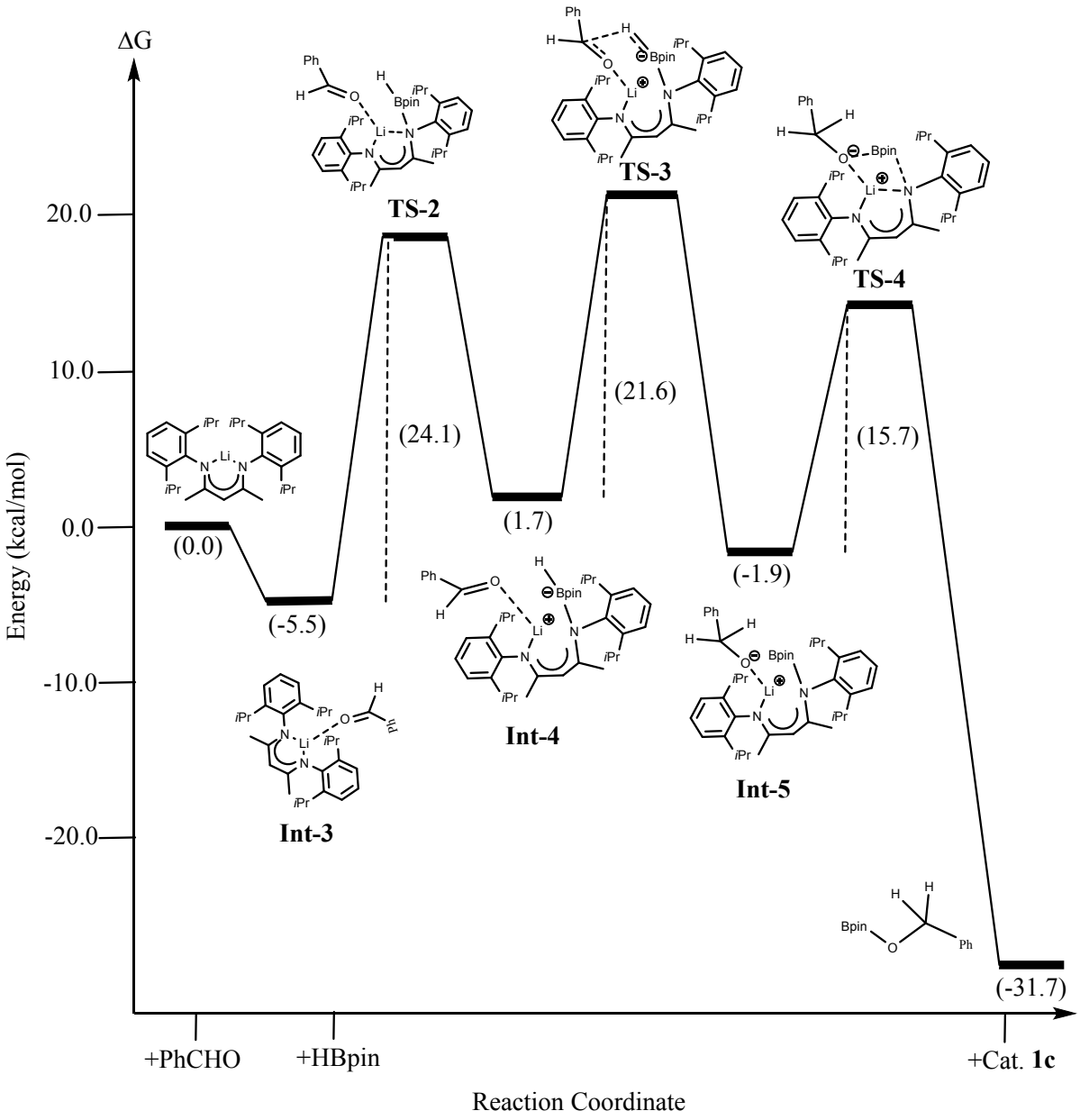


Figure S3. Thereaction energy profile diagram for the catalytic aldehyde hydroboration by catalyst **1c**. The values (in kcal/mol) have been calculated at the PBE/TZVP level of theory with DFT.

References:

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

For catalyst 1a

PhCHO

C	-2.223301	0.008658	-0.087980
H	-1.809252	0.855410	0.512190
C	-3.693609	-0.099518	-0.058720
C	-4.363771	-1.133269	-0.740033
C	-4.427942	0.853184	0.669034
C	-5.753162	-1.208730	-0.686099
H	-3.779973	-1.864076	-1.303739
C	-5.820695	0.776860	0.717768
H	-3.899138	1.654383	1.192422
C	-6.481246	-0.254517	0.041134
H	-6.279238	-2.008602	-1.210102
H	-6.392836	1.517089	1.279782
H	-7.570654	-0.317006	0.077968
O	-1.470702	-0.741633	-0.701942

HBpin

C	-2.385032	-0.548218	-0.040641
C	-0.810668	-0.544753	0.029229
O	-2.690084	0.845887	-0.448060
O	-0.507005	0.879191	0.315240
B	-1.599123	1.605301	-0.096725
H	-1.600670	2.801805	-0.145520
C	-3.052654	-0.754083	1.319255
H	-4.130005	-0.561912	1.222218
H	-2.917585	-1.785762	1.672278
H	-2.646104	-0.067650	2.075591
C	-2.973667	-1.493766	-1.076484
H	-2.699138	-2.532412	-0.841022
H	-4.070136	-1.420342	-1.062960

H	-2.621854	-1.259643	-2.088705
C	-0.219451	-1.396941	1.142520
H	-0.490693	-2.453041	0.998056
H	0.876964	-1.322368	1.121814
H	-0.571338	-1.077295	2.130911
C	-0.143078	-0.865898	-1.308181
H	0.933512	-0.662136	-1.227729
H	-0.274443	-1.924559	-1.570756
H	-0.552213	-0.248403	-2.120497

Catalyst **1a**

Li	6.322742	13.925952	0.417046
O	4.726484	13.347082	0.665172
C	3.509305	12.892784	0.860581
C	2.694398	13.411950	1.934236
C	1.416069	12.875585	2.134639
C	0.898789	11.864755	1.321455
C	1.674077	11.381492	0.265128
C	2.960854	11.868648	0.002350
C	3.218104	14.542018	2.842878
C	4.474084	14.071470	3.611879
C	3.773502	11.323336	-1.189995
C	2.998941	10.265624	-1.999283
C	2.184347	14.980004	3.898099
C	3.547075	15.792691	1.994905
C	4.113598	12.472886	-2.167212
C	5.069576	10.645529	-0.689321
H	0.795077	13.253496	2.948373
H	-0.100848	11.463667	1.504139
H	1.253278	10.601213	-0.370746
H	2.611921	15.793511	4.504525
H	1.918763	14.159662	4.581849
H	1.260485	15.360135	3.435982
H	4.268574	15.553753	1.204710
H	3.965230	16.588754	2.632423
H	2.633017	16.182483	1.520738
H	5.251421	13.724443	2.920341
H	4.219451	13.240833	4.287714
H	4.880927	14.894536	4.221593
H	3.190693	12.897360	-2.591755
H	4.731774	12.098021	-2.999464
H	4.655724	13.277189	-1.654851
H	5.669871	11.340761	-0.089994
H	5.673910	10.295219	-1.542370
H	4.827237	9.773386	-0.062627
H	2.749795	9.382058	-1.392294
H	3.624144	9.926853	-2.840001
H	2.066212	10.670865	-2.419942

Int 1

C	-0.755767	-3.508899	-0.980590
C	-0.872232	-2.337063	-0.144000
C	-1.279719	-2.502670	1.232638
C	-1.561314	-3.790808	1.706267
C	-1.456753	-4.920944	0.891995
C	-1.054805	-4.764224	-0.436820
O	-0.610949	-1.145176	-0.627477
Li	-0.373397	0.495554	-1.066820
C	-1.400584	-1.283026	2.169069
C	-2.464255	-0.297974	1.630791
C	-0.302956	-3.378670	-2.449080
C	1.114890	-2.763542	-2.509159
C	-0.030170	-0.577515	2.297434
C	-1.836545	-1.671494	3.594793
C	-0.234272	-4.738506	-3.170594
C	-1.298880	-2.498678	-3.239290
O	0.699921	2.040036	-0.640864
C	2.193450	2.147259	-0.748694
C	2.799921	0.770939	-0.530365
B	0.258865	3.226241	-0.063069
O	1.265924	4.005045	0.425500
C	2.511713	3.197323	0.375673
C	2.673354	2.571026	1.760279
C	3.673842	4.125678	0.058450
C	2.477578	2.655855	-2.159663
H	-1.871800	-3.927163	2.743106
H	-1.684303	-5.912921	1.289022
H	-0.973486	-5.655304	-1.061020
H	-1.899753	-0.762030	4.212015
H	-1.116367	-2.351409	4.075136
H	-2.826718	-2.152089	3.606573
H	-2.242347	0.002886	0.599347
H	-2.509268	0.603823	2.262611
H	-3.458564	-0.770577	1.637319
H	0.356043	-0.288280	1.312963
H	0.703576	-1.250517	2.767562
H	-0.117384	0.324999	2.924687
H	-2.294607	-2.968425	-3.255476
H	-0.960680	-2.380455	-4.281932
H	-1.391857	-1.507224	-2.780318
H	1.137579	-1.793177	-1.998827
H	1.430478	-2.625380	-3.556303
H	1.841638	-3.429187	-2.018072
H	0.481966	-5.424308	-2.692473
H	0.099628	-4.579098	-4.207581
H	-1.215459	-5.235381	-3.208517
H	-0.900099	3.510609	-0.007089
H	3.559461	2.717166	-2.337660

H	2.050950	1.956826	-2.892383
H	2.037192	3.648521	-2.329069
H	3.820744	4.826242	0.891449
H	4.599761	3.545669	-0.065760
H	3.496123	4.704632	-0.855797
H	2.529788	0.098364	-1.357821
H	3.896288	0.847667	-0.514161
H	2.468865	0.314456	0.409825
H	3.613825	2.008399	1.829979
H	2.693502	3.370970	2.512873
H	1.840525	1.894526	1.999088

TS 1

C	-0.917651	-3.633520	-1.045322
C	-0.843454	-2.496806	-0.157360
C	-1.360928	-2.623907	1.186867
C	-1.945292	-3.835079	1.574946
C	-2.035925	-4.925880	0.706293
C	-1.517001	-4.812271	-0.586443
O	-0.303154	-1.373248	-0.565235
Li	0.178152	0.269968	-0.597113
C	-1.266334	-1.446822	2.179266
C	-2.082642	-0.244782	1.653490
C	-0.332703	-3.551300	-2.469503
C	1.182040	-3.245707	-2.399403
C	0.213902	-1.054348	2.403117
C	-1.839520	-1.792522	3.567690
C	-0.494394	-4.869638	-3.250355
C	-1.053218	-2.450621	-3.280900
O	0.797257	2.009506	-0.632827
C	2.226233	2.336502	-0.760449
C	3.033401	1.092487	-0.410659
B	0.114177	3.257892	-0.243800
O	1.108332	4.236739	0.067962
C	2.362526	3.524278	0.259318
C	2.442374	3.043155	1.713278
O	-0.874013	3.725734	-1.322058
C	-1.934725	3.445003	-0.582693
C	-2.838696	2.377391	-0.912297
C	-4.030036	2.234063	-0.163773
C	-4.895586	1.181841	-0.438712
C	-4.576600	0.264139	-1.450577
C	-3.399467	0.402283	-2.201932
C	-2.527351	1.450912	-1.936615
C	3.510627	4.478512	-0.047692
C	2.484510	2.758911	-2.208391
H	-2.344075	-3.942526	2.584619
H	-2.499009	-5.858563	1.036371
H	-1.584745	-5.677005	-1.248416

H	-1.738696	-0.915999	4.226345
H	-1.300608	-2.628172	4.039049
H	-2.907746	-2.051878	3.519253
H	-1.822858	0.004585	0.617615
H	-1.922665	0.644435	2.284527
H	-3.156761	-0.482656	1.662537
H	0.732265	-0.862470	1.455077
H	0.750530	-1.871414	2.909328
H	0.283463	-0.155553	3.037036
H	-2.124507	-2.687437	-3.378464
H	-0.624313	-2.379507	-4.293934
H	-0.955181	-1.479522	-2.782029
H	1.362877	-2.307219	-1.861380
H	1.602349	-3.163124	-3.415200
H	1.711885	-4.056890	-1.876441
H	0.022863	-5.707104	-2.757649
H	-0.055576	-4.749546	-4.252792
H	-1.552160	-5.145912	-3.379976
H	-0.694687	2.954880	0.719526
H	3.554287	2.939416	-2.384970
H	2.157829	1.953647	-2.882236
H	1.925949	3.670380	-2.461279
H	3.543786	5.273173	0.711164
H	4.472515	3.945331	-0.025243
H	3.388156	4.946550	-1.032280
H	2.886503	0.310242	-1.172769
H	4.107638	1.325062	-0.391206
H	2.754895	0.686597	0.571197
H	3.410418	2.569711	1.930276
H	2.327117	3.910322	2.378226
H	1.641431	2.325770	1.942518
H	-1.610311	1.584757	-2.513654
H	-3.163478	-0.320672	-2.982707
H	-5.251604	-0.568636	-1.655681
H	-5.814043	1.062749	0.137349
H	-4.255822	2.948949	0.630348
H	-2.263672	4.175212	0.171892

Pdt

C	-2.922920	-0.517136	0.163781
C	-1.541987	-0.434909	-0.034209
C	-0.913017	0.814767	-0.144750
C	-1.690508	1.978137	-0.053818
C	-3.071793	1.897729	0.154623
C	-3.691691	0.649012	0.262831
H	-3.401479	-1.495636	0.244267
H	-0.944778	-1.345181	-0.115047
H	-1.211670	2.956219	-0.150234
H	-3.664725	2.812304	0.222251

H	-4.770242	0.583151	0.418919
C	0.582403	0.918569	-0.312540
H	0.856624	1.919924	-0.677526
H	1.083460	0.768080	0.659602
O	1.062563	-0.098749	-1.218890
C	3.876237	-0.242167	-3.437771
C	3.736977	1.308926	-3.186364
O	2.591356	-0.758267	-2.937242
O	2.866879	1.354166	-1.997941
B	2.141365	0.173290	-2.015595
C	5.040616	2.022078	-2.860795
H	5.750099	1.920558	-3.694985
H	4.848651	3.093272	-2.705269
H	5.505367	1.618765	-1.952887
C	2.989542	2.032468	-4.308102
H	2.750247	3.051778	-3.975142

For catalyst **1c**

N	11.345787	1.032024	3.834288
C	11.508810	-0.283612	3.982117
Li	12.831373	2.169830	3.491157
C	12.759553	-0.936369	3.867205
H	12.735722	-2.017591	4.006193
C	10.305808	-1.152739	4.292972
H	9.820397	-0.821810	5.224557
H	10.584126	-2.208091	4.397364
H	9.545371	-1.066468	3.500764
C	10.059245	1.618389	3.929212
C	9.259924	1.754465	2.762286
C	8.051498	2.458050	2.849721
H	7.428633	2.570983	1.959605
C	7.627716	3.023560	4.055211
H	6.682696	3.569418	4.103301
C	8.415785	2.879956	5.198117
H	8.080619	3.322455	6.139439
C	9.630571	2.180753	5.158852
C	10.495226	2.061557	6.406546
H	11.265157	1.304800	6.195869
C	9.705345	1.593398	7.637793
H	9.186472	0.643162	7.440269
H	8.949705	2.332896	7.943874
H	10.383930	1.440836	8.490816
C	11.223226	3.387647	6.692633
H	11.821685	3.711954	5.827582
H	11.901995	3.284502	7.553264
H	10.502546	4.189149	6.917167
C	9.744452	1.187279	1.433853
H	10.444952	0.370497	1.663115
C	8.619021	0.603885	0.567925

H	9.043302	0.111108	-0.319819
H	7.927357	1.382358	0.210871
H	8.031742	-0.141050	1.125134
C	10.536370	2.251968	0.651433
H	11.380589	2.640335	1.241888
H	9.889992	3.104873	0.392026
H	10.945471	1.832067	-0.280430
N	14.257879	0.914025	3.412795
C	14.036360	-0.388959	3.595608
C	15.196181	-1.362786	3.511857
H	15.693310	-1.289295	2.532125
H	14.866424	-2.397756	3.661529
H	15.961778	-1.125043	4.266554
C	15.567284	1.397099	3.164284
C	16.406722	1.754768	4.254048
C	17.650039	2.341512	3.984924
H	18.302722	2.623948	4.814363
C	18.070764	2.579991	2.673963
H	19.044579	3.037116	2.484258
C	17.239271	2.228698	1.609875
H	17.569192	2.420102	0.585407
C	15.985920	1.639810	1.830558
C	15.082728	1.296776	0.653675
H	14.215817	0.753098	1.058487
C	15.774064	0.380520	-0.368700
H	16.143169	-0.540533	0.107016
H	16.632166	0.880492	-0.843856
H	15.070396	0.095223	-1.165658
C	14.553130	2.574682	-0.022556
H	14.026340	3.220167	0.697562
H	13.850140	2.326253	-0.832227
H	15.377951	3.163169	-0.454251
C	15.932465	1.554866	5.687674
H	15.124057	0.808801	5.664840
C	17.027615	1.025093	6.624422
H	16.604651	0.810004	7.617328
H	17.838544	1.756103	6.764832
H	17.472144	0.097631	6.233858
C	15.325983	2.859252	6.238049
H	14.510247	3.224808	5.595575
H	16.088976	3.651626	6.292274
H	14.916523	2.706125	7.248546

Int 2

C	17.526398	3.953258	2.375161
C	16.857717	5.064917	2.959499
C	16.324242	6.088004	2.129168
C	16.445169	5.967375	0.737725
C	17.081504	4.868285	0.156943

C	17.621741	3.875618	0.978545
N	16.559359	5.059354	4.338886
C	17.394342	5.548612	5.252460
C	18.703287	6.173717	4.809997
C	15.596333	7.281282	2.732961
C	16.234654	8.615705	2.313676
C	18.072670	2.829835	3.246954
C	19.518396	2.452941	2.889120
C	17.126696	5.513414	6.641505
C	15.993841	4.994026	7.316472
C	16.012382	5.056526	8.833182
N	14.945734	4.457341	6.693439
C	13.831375	3.980816	7.425204
C	13.691808	2.588256	7.656111
C	12.532031	2.115778	8.286956
C	11.517131	2.988589	8.680820
C	11.651698	4.357614	8.432047
C	12.791618	4.874709	7.803210
C	14.765092	1.611872	7.195313
C	15.310156	0.752998	8.346836
C	12.890157	6.353930	7.452894
C	12.296188	7.283948	8.519417
C	14.245867	0.731035	6.044415
C	12.244091	6.613829	6.078536
C	14.096578	7.258074	2.388460
C	17.152543	1.596053	3.192366
Li	14.863378	4.266341	4.784123
O	13.730183	3.492380	3.414575
C	13.933524	3.395310	2.194650
C	13.007835	2.782509	1.247936
C	11.781386	2.227836	1.666183
C	10.928213	1.659162	0.725977
C	11.291409	1.639862	-0.630504
C	12.509445	2.187812	-1.051213
C	13.368859	2.758890	-0.113339
H	17.902755	5.934442	7.281410
H	15.167106	5.650910	9.213893
H	16.944691	5.494786	9.209187
H	15.898627	4.047722	9.260305
H	12.420160	1.043553	8.469040
H	10.621471	2.605301	9.174987
H	10.847188	5.034333	8.728490
H	13.957870	6.600320	7.354958
H	12.737625	7.092389	9.509143
H	11.204911	7.168237	8.607027
H	12.493392	8.334120	8.255926
H	12.696235	5.982634	5.298613
H	12.370905	7.665179	5.777194
H	11.166248	6.389855	6.108115
H	15.600435	2.212989	6.804136

H	16.127007	0.105469	7.992247
H	14.528649	0.102674	8.769645
H	15.701350	1.382167	9.160322
H	13.875828	1.344198	5.208334
H	13.415684	0.090615	6.381734
H	15.045452	0.077016	5.663359
H	19.274957	6.565889	5.659918
H	18.517857	6.993518	4.098834
H	19.326625	5.436486	4.279516
H	16.025362	6.745326	0.094330
H	17.160698	4.787358	-0.929357
H	18.120767	3.016712	0.522596
H	18.068146	3.190846	4.285989
H	20.179100	3.332034	2.926266
H	19.589752	2.019061	1.879649
H	19.903896	1.704744	3.598399
H	16.134138	1.841869	3.527794
H	17.535177	0.794632	3.843191
H	17.084108	1.201453	2.166362
H	15.684111	7.194139	3.826461
H	15.735917	9.455828	2.820763
H	16.148122	8.781398	1.228370
H	17.303261	8.645076	2.573792
H	13.619996	6.330128	2.736782
H	13.937697	7.330002	1.300975
H	13.576043	8.102616	2.865236
H	11.519412	2.253828	2.725581
H	14.323783	3.193243	-0.422921
H	12.784377	2.168146	-2.106984
H	10.617312	1.192672	-1.363790
H	9.976809	1.226991	1.040555
H	14.873587	3.793300	1.757200

TS 2

C	17.735349	4.474819	5.006674
N	16.729900	5.198043	4.465647
Li	14.648096	4.247849	4.945112
B	15.829040	4.318621	2.719811
H	16.494642	3.336510	2.920811
O	16.018388	5.097049	1.564157
C	16.788024	6.630119	4.502619
C	16.491448	9.441813	4.477714
H	18.447106	5.747986	2.602616
C	15.937704	8.686232	5.510787
C	19.054910	5.139330	5.366114
C	19.890018	7.343214	2.901541
C	18.474552	6.845118	2.526998
C	18.214531	7.223648	1.060154
C	14.688048	6.623898	0.185234

C	14.705685	5.309084	0.955062
C	13.674022	6.633723	2.904974
C	13.749976	5.279598	2.193959
C	14.465712	4.135627	-0.004374
C	12.349879	4.748717	1.911069
C	14.981593	-0.111271	2.996525
C	13.960804	0.923992	3.501645
O	12.869516	4.638994	5.665408
C	13.684905	0.765614	4.989896
C	11.707781	5.034389	5.772792
C	14.398808	1.544749	5.940459
N	15.359376	2.488446	5.496845
C	16.645153	2.177745	5.515216
C	14.239902	7.111628	7.325412
C	15.542619	6.532747	6.757674
C	17.705474	3.092778	5.258512
C	16.609597	6.444153	7.867063
H	13.810669	6.418572	8.063326
C	13.766295	3.342178	8.950700
C	17.109658	0.796604	5.956277
C	14.764847	2.335958	8.353124
C	14.084732	1.445460	7.321768
C	13.108771	0.525642	7.730779
C	12.446730	-0.287187	6.809992
C	12.734072	-0.156642	5.449757
C	10.534557	4.165714	5.839074
C	9.255406	4.753942	5.870163
C	8.119438	3.945863	5.897128
C	8.260649	2.552191	5.900093
C	9.534457	1.963718	5.877263
C	10.671896	2.763726	5.846120
H	9.161518	5.843238	5.865477
H	11.932080	1.593882	3.024988
H	12.914510	1.143041	1.609468
C	12.681562	0.879971	2.652956
H	12.224125	-0.121789	2.642878
H	11.750566	4.765001	2.832101
H	12.378379	3.716431	1.543764
H	11.843774	5.379154	1.165179
H	14.436434	3.180511	0.539613
H	13.525445	4.253623	-0.561182
H	15.293789	4.095262	-0.725992
H	15.364217	6.563268	-0.679453
H	15.001269	7.466628	0.813192
H	13.674671	6.824403	-0.193310
H	17.246710	6.845020	0.725495
H	18.997423	6.788155	0.419490
H	18.244457	8.315114	0.917164
H	17.745061	9.400830	2.734857
H	19.977355	8.422368	2.698965

H	20.648907	6.826544	2.293731
H	20.130934	7.185453	3.960005
H	19.760389	5.054763	4.524906
H	18.927287	6.206616	5.582658
H	19.514463	4.654774	6.236342
H	15.540356	2.912761	7.828050
H	17.388361	0.816454	7.021970
H	18.000516	0.487176	5.392723
H	14.411404	8.070554	7.837754
H	18.688017	2.675184	5.493260
H	15.347955	5.494910	6.452060
H	13.494700	7.278210	6.535034
H	16.222471	5.873210	8.725696
H	17.520949	5.945971	7.510957
H	16.884371	7.450828	8.218724
H	12.964322	2.824706	9.500088
H	13.299695	3.946714	8.160660
H	16.324875	0.040536	5.835486
H	14.273712	4.022918	9.652519
H	16.166899	0.800064	9.049425
H	15.999522	2.194296	10.145862
H	14.717724	0.965843	10.065801
H	12.862737	0.442909	8.792842
H	11.698030	-1.007231	7.148259
H	12.193970	-0.773850	4.728147
H	11.669325	2.321306	5.828620
H	14.606323	-1.137004	3.142145
H	15.175012	0.032246	1.921711
H	15.940146	-0.021130	3.525619
H	14.409330	1.919092	3.369916
O	14.437993	4.313414	3.055271
H	13.200476	6.507460	3.887721
H	14.670378	7.064848	3.062501
H	7.125635	4.396265	5.915792
H	7.371669	1.918610	5.921384
H	9.637626	0.877347	5.884881
H	13.067455	7.342832	2.324675
H	16.351696	10.524810	4.448119
C	17.257721	8.801916	3.507832
C	17.451252	7.410686	3.510187
H	11.495641	6.128082	5.814129
H	15.384303	9.192419	6.303893
C	15.451673	1.525251	9.464565
C	16.081402	7.293586	5.550797

Int 3

C	17.906593	4.556155	5.004687
N	17.023036	5.323101	4.304958
Li	14.182722	4.086887	5.244904

B	16.003970	4.726192	3.235758
H	16.298529	3.538772	3.132177
O	16.076763	5.483533	1.976805
C	17.087047	6.759611	4.460041
C	17.021575	9.551115	4.759633
H	18.568784	5.931528	2.440715
C	16.399613	8.731971	5.700739
C	19.230761	5.192927	5.385686
C	20.143831	7.398689	2.687199
C	18.668222	7.026454	2.428305
C	18.261780	7.517604	1.030574
C	14.646447	6.620311	0.388443
C	14.766149	5.481302	1.398721
C	13.744676	7.110397	3.117340
C	13.839424	5.650641	2.656332
C	14.533125	4.139143	0.680441
C	12.435391	5.071415	2.483223
C	15.115274	0.204338	3.011454
C	14.018873	1.138024	3.556189
O	12.540945	4.513392	6.084416
C	13.750319	0.882901	5.033632
C	11.363537	4.860536	6.205927
C	14.481207	1.589897	6.025899
N	15.420694	2.577637	5.618646
C	16.707702	2.293351	5.603636
C	14.410590	7.038329	7.129098
C	15.761850	6.484131	6.654548
C	17.780396	3.211141	5.355541
C	16.702373	6.293210	7.860240
H	13.926905	6.321560	7.808519
C	13.919000	3.205159	9.146439
C	17.199284	0.909895	6.008303
C	14.895054	2.221412	8.476818
C	14.189709	1.405039	7.401928
C	13.210212	0.469276	7.762804
C	12.527890	-0.274085	6.799284
C	12.798555	-0.060602	5.445879
C	10.216135	3.989178	5.968652
C	8.921272	4.541491	5.995142
C	7.816291	3.731741	5.734719
C	8.002482	2.370428	5.463147
C	9.291196	1.814059	5.450589
C	10.397988	2.618421	5.698060
H	8.791870	5.605439	6.210113
H	11.944738	1.672974	3.085321
H	12.976437	1.375242	1.665138
C	12.755021	1.042169	2.690073
H	12.378448	0.009768	2.623227
H	11.825278	5.273676	3.375404
H	12.468228	3.985777	2.329232

H	11.929742	5.534118	1.622237
H	14.577908	3.301167	1.389464
H	13.565339	4.110568	0.159192
H	15.331998	4.000037	-0.062212
H	15.301874	6.425532	-0.473062
H	14.937973	7.580398	0.832462
H	13.613585	6.703241	0.017352
H	17.232560	7.218767	0.811469
H	18.925413	7.079955	0.268346
H	18.345912	8.613367	0.951908
H	18.222676	9.616817	2.977298
H	20.296131	8.484329	2.581195
H	20.795337	6.897117	1.955045
H	20.476919	7.114239	3.694522
H	19.890300	5.225700	4.504627
H	19.105149	6.228349	5.725788
H	19.733708	4.622219	6.174413
H	15.674170	2.818462	7.980463
H	17.589171	0.938342	7.038207
H	18.025042	0.588838	5.358294
H	14.533162	7.983005	7.680111
H	18.737801	2.781126	5.662703
H	15.601590	5.485724	6.221454
H	13.730602	7.218776	6.285571
H	16.225772	5.652113	8.618308
H	17.649722	5.821968	7.566713
H	16.932870	7.262996	8.328547
H	13.113519	2.666108	9.668943
H	13.453419	3.868548	8.403867
H	16.399922	0.161108	5.973517
H	14.445445	3.829613	9.884958
H	16.278042	0.623335	9.061567
H	16.150575	1.955193	10.238278
H	14.846574	0.755294	10.108587
H	12.978103	0.318355	8.820241
H	11.775603	-1.006785	7.099875
H	12.243008	-0.625918	4.694712
H	11.405696	2.198383	5.698441
H	14.810336	-0.850410	3.101698
H	15.305900	0.417272	1.948023
H	16.060400	0.334878	3.555061
H	14.412605	2.165814	3.475651
O	14.554919	4.887760	3.652413
H	13.275420	7.137161	4.111244
H	14.741984	7.562164	3.197782
H	6.810944	4.155908	5.744817
H	7.136977	1.735716	5.263056
H	9.425493	0.749528	5.249001
H	13.128695	7.711543	2.432220
H	16.986411	10.637712	4.867143

C	17.706683	8.972737	3.693589
C	17.774622	7.580226	3.531277
H	11.129206	5.906105	6.508960
H	15.886932	9.187777	6.550050
C	15.581829	1.334983	9.528723
C	16.416888	7.336217	5.572508

TS 2

C	14.082091	1.347943	3.089466
C	12.919227	2.030550	3.468208
C	11.666773	1.447880	3.147494
C	11.599902	0.220894	2.469796
C	12.779120	-0.439013	2.099849
C	14.019844	0.128792	2.410991
C	13.070224	3.437410	4.088218
O	14.247591	4.156614	3.977122
Li	14.982063	4.082105	5.541718
O	13.540732	5.131459	6.338727
C	12.668449	5.947408	7.180581
C	12.317776	7.233108	6.446344
B	13.196175	3.751721	6.553561
O	12.087529	3.698617	7.414517
C	11.449274	4.989373	7.405127
C	10.740761	5.146670	8.741795
N	14.391727	2.758227	6.775156
C	14.314969	1.316019	6.473573
C	15.497963	0.672017	5.997261
C	15.442127	-0.670425	5.601880
C	14.253602	-1.390349	5.620659
C	13.126418	-0.786155	6.154001
C	13.144587	0.525380	6.659009
C	16.859721	1.348166	5.921117
C	17.670458	0.922381	4.687194
C	11.921115	0.898833	7.490790
C	10.639599	1.015863	6.654936
C	15.105443	3.066302	7.985499
C	14.664482	2.289669	9.193189
C	16.119542	3.970173	8.135049
C	16.956727	4.809909	7.265097
C	18.305407	5.123594	7.874022
N	16.600791	5.208604	6.078488
C	17.407951	6.137232	5.341975
C	18.345476	5.692538	4.379418
C	19.078069	6.642697	3.650877
C	18.907540	8.009327	3.856373
C	17.961306	8.439950	4.785608
C	17.187470	7.531424	5.521646
C	18.548352	4.220149	4.073488
C	17.857225	3.864767	2.743653

C	16.131082	8.049128	6.486146
C	15.396486	9.288501	5.952621
C	16.715475	8.349891	7.878132
C	20.032928	3.823068	4.065792
C	17.692107	1.052971	7.185889
C	11.726531	-0.101217	8.647499
C	10.425596	5.029306	6.265661
C	13.411743	6.247682	8.482572
H	16.478204	4.012683	9.164919
H	13.609234	2.518611	9.408882
H	15.277335	2.524388	10.069312
H	14.723578	1.208018	9.001322
H	16.346844	-1.154540	5.234768
H	14.216548	-2.416543	5.249056
H	12.202243	-1.360695	6.238768
H	12.088351	1.874158	7.944302
H	12.646008	-0.208306	9.242584
H	11.437564	-1.101471	8.290969
H	10.928495	0.257713	9.316344
H	10.737013	1.800871	5.894385
H	9.788059	1.278605	7.301479
H	10.399855	0.072161	6.139733
H	16.691231	2.433815	5.862127
H	18.646662	1.600560	7.153770
H	17.919903	-0.023218	7.241497
H	17.166805	1.340656	8.104704
H	17.107281	1.062857	3.754839
H	17.973162	-0.132571	4.744205
H	18.593766	1.510675	4.624849
H	18.918423	4.206597	7.848875
H	18.215804	5.412216	8.929950
H	18.835068	5.904953	7.318655
H	17.809508	9.511031	4.932287
H	19.496368	8.733618	3.288630
H	19.798488	6.300386	2.904356
H	18.052133	3.648697	4.869403
H	20.517780	4.077322	5.020379
H	20.584498	4.327946	3.259214
H	20.144391	2.740358	3.904547
H	16.770869	4.029614	2.816367
H	18.027686	2.809763	2.483568
H	18.254836	4.483562	1.923885
H	15.394504	7.237896	6.591009
H	15.928542	8.715077	8.556107
H	17.491772	9.128348	7.809549
H	17.168771	7.461959	8.336531
H	14.974420	9.109770	4.952529
H	16.060049	10.164196	5.892025
H	14.574004	9.559808	6.631515
H	10.733514	1.953603	3.413894

H	15.033440	1.823834	3.329327
H	14.941022	-0.382686	2.120717
H	12.731690	-1.391508	1.566684
H	10.629277	-0.221194	2.218578
H	12.132829	4.018736	3.906554
H	12.701503	3.256681	5.396517
H	9.761319	4.159261	6.360843
H	9.818075	5.941977	6.319343
H	10.900447	4.994958	5.276146
H	10.328835	6.159876	8.836655
H	9.911093	4.428124	8.799067
H	11.419748	4.957020	9.582288
H	14.370927	6.730048	8.257680
H	12.824927	6.923840	9.118354
H	13.622876	5.325622	9.039992
H	11.570954	7.803059	7.019004
H	13.209058	7.860517	6.332354
H	11.915583	7.027429	5.447090

Int 4

C	13.261736	1.402474	3.510509
C	12.009109	1.907741	3.146321
C	10.945405	1.003256	2.988396
C	11.127813	-0.367285	3.189902
C	12.386351	-0.861170	3.559617
C	13.451483	0.030711	3.716882
C	11.785756	3.409721	2.950745
O	12.913661	4.174954	2.858869
Li	14.437946	4.874283	3.136346
N	13.871596	4.078797	7.280495
B	12.728028	3.271939	7.690974
O	12.785659	2.503120	8.841251
C	11.411138	2.025689	9.074467
C	10.756276	3.029879	10.025524
C	13.797595	5.104506	6.333950
C	12.419621	5.684467	6.111709
C	14.800910	5.634954	5.563287
C	16.185384	5.306304	5.163140
C	17.333696	5.182222	6.121031
N	16.321103	5.256485	3.861968
C	17.578852	5.199869	3.202753
C	17.901259	4.045104	2.449485
C	19.105459	4.027320	1.732288
C	19.960518	5.128602	1.731323
C	19.606972	6.278702	2.439582
C	18.416218	6.347919	3.174932
C	16.924609	2.881860	2.350789
C	16.054743	3.030737	1.087110
C	17.980937	7.650514	3.836931

C	16.968132	8.378761	2.931235
C	19.141059	8.578979	4.216028
C	17.595992	1.502433	2.380154
C	15.087786	3.853436	8.030156
C	15.812225	2.654552	7.851620
C	16.962473	2.456503	8.630902
C	17.382829	3.412211	9.555375
C	16.638870	4.578553	9.733595
C	15.472844	4.815240	8.992556
C	15.416981	1.595511	6.833177
C	15.063520	0.262928	7.514180
C	14.635989	6.050772	9.292432
C	14.015842	5.945775	10.698089
C	16.527194	1.392650	5.789933
C	15.432549	7.354068	9.123876
C	10.799834	2.056041	7.626043
C	11.117401	0.803913	6.809941
C	11.474414	0.645596	9.712114
O	11.537833	3.168990	7.002889
C	9.313775	2.375498	7.564160
H	14.424051	6.436670	4.918574
H	11.827097	5.013899	5.474590
H	12.494245	6.654742	5.607749
H	11.876792	5.810948	7.058847
H	17.543205	1.540420	8.504760
H	18.286340	3.243139	10.144989
H	16.958567	5.312150	10.476964
H	13.805016	6.083335	8.575871
H	15.824164	7.446369	8.100198
H	16.281832	7.404990	9.822165
H	14.785807	8.222390	9.319410
H	13.424943	5.023357	10.797223
H	13.353837	6.803690	10.890061
H	14.794330	5.936269	11.476717
H	14.522543	1.951368	6.297502
H	16.208095	0.672487	5.023817
H	17.445164	1.001075	6.253253
H	16.781369	2.333864	5.284361
H	14.291187	0.409056	8.281196
H	15.948312	-0.180333	7.996660
H	14.689066	-0.457128	6.770881
H	17.245102	4.269691	6.723220
H	17.325986	6.019774	6.833203
H	18.291026	5.157734	5.587383
H	20.269056	7.145149	2.411342
H	20.897691	5.096386	1.171733
H	19.373149	3.139100	1.156859
H	16.257068	2.935566	3.224769
H	18.242981	1.386836	3.261243
H	18.206775	1.328489	1.481557

H	16.829102	0.713810	2.411558
H	15.561484	4.013866	1.039091
H	15.269195	2.260813	1.061509
H	16.675394	2.930570	0.183342
H	17.456628	7.405499	4.771823
H	18.757752	9.435307	4.790134
H	19.652162	8.983213	3.329084
H	19.888379	8.059741	4.834604
H	16.104655	7.736177	2.704899
H	17.440048	8.663891	1.978186
H	16.598198	9.292863	3.420052
H	9.960195	1.382386	2.697288
H	14.085918	2.109484	3.624398
H	14.437079	-0.348233	3.998858
H	12.534353	-1.931850	3.717091
H	10.288081	-1.054431	3.058956
H	11.122344	3.503961	2.053008
H	11.127360	3.713490	3.809293
H	11.944078	0.716560	10.703192
H	10.460441	0.240278	9.842572
H	12.054946	-0.056860	9.102332
H	9.741457	2.713263	10.302713
H	11.359507	3.099319	10.941187
H	10.699504	4.030608	9.572661
H	8.984769	2.384759	6.515524
H	8.733928	1.608091	8.097060
H	9.091362	3.355089	8.004971
H	10.535700	-0.058605	7.164094
H	10.866410	0.987781	5.757656
H	12.185353	0.551402	6.856427

TS 4

C	15.953467	5.789178	1.352104
C	14.786609	6.121210	2.104280
C	13.580106	6.452891	1.429724
C	13.590226	6.504358	0.027641
C	14.737027	6.219493	-0.710729
C	15.909377	5.854271	-0.043968
N	14.872987	5.954658	3.494779
C	14.649482	6.895780	4.389481
C	14.400620	8.341275	4.010121
C	12.260283	6.664125	2.160776
C	11.613867	8.016586	1.814291
C	17.237662	5.406195	2.073975
C	18.041647	6.658442	2.466956
C	14.828158	6.639350	5.784613
C	15.043121	5.499151	6.588800
C	16.090580	5.811743	7.664182
N	14.552594	4.216476	6.505003

C	14.784345	3.389549	7.672190
C	15.553897	2.209397	7.527229
C	15.700093	1.351162	8.621342
C	15.100754	1.641818	9.847523
C	14.380813	2.823729	9.992730
C	14.219121	3.728556	8.931544
C	16.244898	1.901684	6.208084
C	17.590071	2.644905	6.093680
C	13.510081	5.052042	9.231199
C	12.001979	4.899372	9.473037
Li	15.260431	4.309277	4.432833
C	16.417815	0.406568	5.922905
C	14.148116	5.768049	10.439277
C	11.288868	5.507788	1.868803
C	18.108678	4.400710	1.311778
O	13.766999	3.303625	4.126648
B	13.202647	3.313026	5.499770
O	13.051673	1.990244	6.005858
C	11.668051	1.767516	6.367679
C	11.584157	1.627291	7.888437
C	14.078794	2.068561	3.441666
C	13.371970	1.940007	2.112274
C	12.478488	0.883064	1.884783
C	11.832565	0.742148	0.652038
C	12.080009	1.659433	-0.374190
C	12.981741	2.708655	-0.162032
C	13.627114	2.842264	1.069077
O	11.995258	4.047269	5.730950
C	10.933484	3.048999	5.780558
C	9.780223	3.559695	6.639408
C	10.406581	2.843705	4.353280
C	11.218368	0.449390	5.733897
H	15.019370	9.005240	4.629775
H	13.351031	8.617385	4.190880
H	14.626479	8.524990	2.952075
H	12.456544	6.642286	3.241094
H	15.143725	7.545539	6.309361
H	17.473474	3.728142	6.249542
H	16.233637	5.018014	8.400711
H	15.838924	6.740789	8.192328
H	17.052910	5.985047	7.158883
H	18.298099	2.282582	6.854260
H	18.045651	2.481174	5.103565
H	18.935531	6.383147	3.048016
H	17.433676	7.344134	3.074101
H	18.370291	7.198443	1.565390
H	16.939679	4.923817	3.023913
H	12.303053	8.855358	1.988122
H	11.304194	8.050338	0.758298
H	17.528820	3.516666	1.006482

H	10.341594	5.662384	2.408122
H	11.716567	4.550240	2.189604
H	11.063615	5.440799	0.793055
H	18.939113	4.063290	1.950066
H	18.552089	4.845099	0.408075
H	12.665592	6.752505	-0.499233
H	16.801380	5.610769	-0.624086
H	14.715973	6.264716	-1.801626
H	15.580393	2.282302	5.421345
H	15.241176	5.832294	10.357237
H	15.209922	0.955653	10.690414
H	13.935060	3.061030	10.961545
H	13.912892	5.244799	11.378609
H	13.748235	6.790080	10.522457
H	13.613935	5.706955	8.356771
H	11.571430	5.863377	9.785053
H	11.788138	4.161026	10.261315
H	11.497463	4.589420	8.552108
H	17.148097	-0.060420	6.601200
H	16.787270	0.261378	4.896626
H	15.459756	-0.122165	6.024106
H	9.395582	4.498881	6.216731
H	12.264076	0.821558	8.200135
H	10.073075	3.741761	7.678331
H	11.907787	2.539349	8.395576
H	10.565111	1.373712	8.215301
H	8.959165	2.826612	6.642637
H	11.819149	-0.373640	6.147674
H	10.029661	3.805796	3.982261
H	9.582978	2.115362	4.326559
H	10.160098	0.247418	5.956904
H	12.285968	0.160219	2.681549
H	11.348052	0.456218	4.645315
H	11.193991	2.511295	3.667406
H	13.832438	1.217492	4.090904
H	15.171665	2.040547	3.256482
H	11.135725	-0.083920	0.494414
H	11.575633	1.554752	-1.337228
H	13.185464	3.430129	-0.955827
H	14.321409	3.669801	1.224248
H	16.286362	0.436735	8.515663
H	10.714472	8.177876	2.427896