Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers

A Silver-Catalyzed Transfer Hydrogenation of Aldehydes in Air and Water

(Supporting Information)

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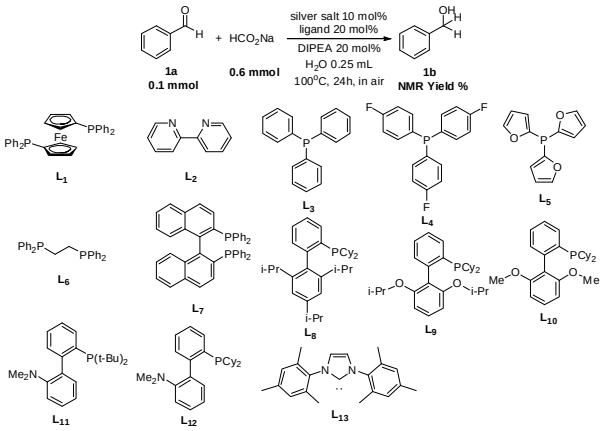
Contents

I. General Information

All transfer hydrogenation reactions were carried out under air. All manipulation and purification procedures were carried out with reagent-grade solvents. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F_{254} precoated plates (0.25 mm). Flash chromatography was performed with Biotage Isolera One Flash Purification System, using Biotage SNAP Ultra 25g prepared column. Nuclear magnetic resonance (NMR) spectra were recorded on Varian MERCURY plus-300 spectrometer (^{1}H 300 MHz, ^{13}C 75 MHz) or a Varian MERCURY plus-400 spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz). Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: δ 77.0 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), and integration.

II. Condition Screening

Table 1. Condition Screening for Aromatic Aldehydes



Silver Salt	Ligand	NMR Yield [a]
$AgPF_6$	L_1	2 %
AgF	L_1	3 %
AgCl	L_1	N.D.
AgBr	L_1	N.D.
AgI	L_1	N.D.
AgOTf	L_1	3 %
AgF	L_2	N.D.
AgF	L_3	N.D.
AgF	L_4	6 %
AgF	L_5	N.D.
AgF	L_6	N.D.
AgF	L_7	N.D.
AgF	L_8	N.D.
AgF	L_9	61 %
AgF	L_{10}	66 %
AgF	L_{11}	50 %
AgF	L_{12}	>99 % (92 %)[b]
AgF	L_{13}	N.D.
$AgPF_6$	L_{12}	38 %
AgCl	L_{12}	85 %
AgBr	L_{12}	11 %
AgI	L_{12}	N.D.
//	L_{12}	N.D.
AgF	//	N.D.
AgF	L_{12}	33 %[c]
AgF	L_{12}	26 %[d]
AgF	L_{12}	80 %[e]
AgF	L_{12}	9 %[f]
AgF	L_{12}	N.D.[g]
AgF	L_{12}	N.D.[h]

[a] ^{1}HNMR yields were determined by using mesitylene as the internal standard;

[b] Isolated Yield;

[c] Reaction was performed without base.

[d] Reaction was carried out without solvent

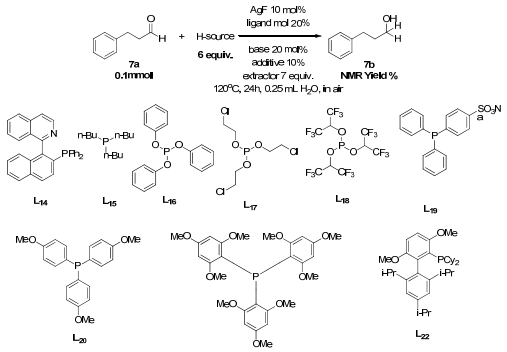
[e] Reaction was carried out in Ethanol

[f] Reaction was carried out in Acetonitrile

[g] Reaction was carried out in Acetone

[h] Reaction was carried out in N-N-dimethylformamide

Table 2. Condition Screening for Aliphatic Aldehydes



H-Source	base	Ligand	additive	extractor	NMR Yield
HCO_2Na	DIPEA	L_{12}	//	//	3 % [a]
HCO_2H	//	L_{12}	//	//	n.d. [a]
HCO_2H·DIPEA	DIPEA	L_{12}	//	//	6 % [a]
HCO_2H·DIPEA	CsF	L_{12}	//	//	7 % [a]
HCO_2H·DIPEA	CsF	L_{12}	LiF	//	n.d. [a]
HCO_2H·DIPEA	CsF	L_{12}	//	//	11 %
HCO_2H·NH_3	CsF	L_{12}	//	//	n.d.
HCO_2H·1/2TMEDA	CsF	L_{12}	//	//	n.d.
HCO_2H·1/2DABCO	CsF	L_{12}	//	//	n.d.
HCO_2H·DBU	CsF	L_{12}	//	//	10 %
HCO_2H·DIPEA	CsF	L_1	//	//	n.d.
HCO_2H·DIPEA	CsF	L_2	//	//	n.d.
HCO_2H·DIPEA	CsF	L_4	//	//	n.d.
HCO_2H·DIPEA	CsF	L_5	//	//	n.d.
HCO_2H·DIPEA	CsF	L_7	//	//	n.d.
HCO_2H·DIPEA	CsF	L_{14}	//	//	n.d.
HCO_2H·DIPEA	CsF	L_8	//	//	trace
HCO_2H·DIPEA	CsF	L_{13}	//	//	n.d.
HCO_2H·DIPEA	CsF	L_{15}	//	//	n.d.
HCO_2H·DIPEA	CsF	L_{16}	//	//	trace
HCO_2H·DIPEA	CsF	L_{17}	//	//	n.d.
HCO_2H·DIPEA	CsF	L_{18}	//	//	n.d.
HCO_2H·DIPEA	CsF	L_{19}	//	//	n.d.
HCO_2H·DIPEA	CsF	L_{20}	//	//	n.d.
HCO_2H·DIPEA	CsF	L_{21}	//	//	n.d.
HCO_2H·DIPEA	CsF	L_{22}	//	//	21 %
HCO_2H·DIPEA	CsF	L_{10}	//	//	15 %
HCO_2H·DIPEA	CsF	L_{10}	//	DIPEA	30 %
HCO_2H·DIPEA	CsF	L_{10}	//	PhCl	30 %
HCO_2H·DIPEA	CsF	L_{10}	TfOH	PhCl	55 %
HCO_2H·DIPEA	CsF	L_{10}	Benzoic Acid	PhCl	12 %
HCO_2H·DIPEA	CsF	L_{10}	CF_3CO_2H	PhCl	11 %
HCO_2H·DIPEA	CsF	L_{10}	TfOH	PhCl	75 % [b]
HCO_2H·DIPEA	CsF	L_{22}	TfOH	PhCl	99 %
HCO_2H·DIPEA	//	L_{10}	TfOH	PhCl	42 %

III. General Procedures

(Synthesis of AgF-DavePhos complex; all the other complexes used in the study were prepared in the same way). An oven-dried reaction vessel, charged with 12.6 mg silver (I) fluoride (0.1 mmol, 1 equiv) and 78.7 mg 2-dicyclohexylphosphino-2'-(N,N-dimethylamino)biphenyl (DavePhos, 0.2 mmol, 2 equiv), is flushed with argon 3 times. 2.5 mL of dry, air-free methylene chloride (DCM) is added into the vessel. The vessel is then sealed and stirred at room temperature. After stirring overnight (12 h), the mixture is stripped of solvent and the resulting solid is kept under vacuum for 1 h before ready to use.

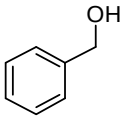
(General Procedures for the Reduction of Aromatic Aldehydes). To a stirred solution of 81.6 mg sodium formate (1.2 mmol, 6 equiv) in 0.5 mL distilled H_2O in air, 9.1 mg of prepared AgF-DavePhos complex (0.02 mmol, 0.1 equiv) is added, along with 20.5 μL of benzaldehyde (0.2 mmol, 1 equiv) and 7 μL of diisopropylethylamine (DIPEA, 0.04 mmol, 0.2 equiv). The vessel is then sealed and stirred at 100°C for 24h. Then, the reaction mixture is cooled to room temperature, extracted with methylene chloride, and the organic phase is washed with brine. The organic phase is then stripped of solvent and the oily crude product is collected. Further purification can be carried out with flash chromatography to give the product in 19.5 mg (92% yield).

(General Procedures for the Reduction of Aliphatic Aldehydes). To a stirred vial of 2 mL H_2O in air, 45μL of formic acid (1.2 mmol, 6 equiv) and 209 μL of diisopropylethylamine (DIPEA, 1.2 mmol, 6 equiv) are added. The mixture is kept stirring until the whole solution is transparent and clear. All the solution is then transferred into a reaction vessel which is charged with 9.5 mg of prepared AgF-SPhos complex (0.02 mmol, 0.1 equiv) and 6.2 mg of cesium fluoride (0.04 mmol, 0.2 equiv) in air. 26.4 μL hydrocinnamaldehyde (0.2 mmol, 1 equiv), 1.8 μL trifluoromethanesulfonic acid (0.02 mmol, 0.1 equiv) and 142 μL chlorobenzene (1.4 mmol, 7 equiv) are then added and the reaction vessel is sealed. The vessel is stirred at 120°C for 24h before cooled down to room temperature. The mixture is extracted with methylene chloride and the resulting organic phase is washed with brine. The solution is then concentrated and subject to flash chromatography to give the desired product in 19.0 mg (71% yield.)

IV. Identification of Products

All compounds are literature known and the data reported herein are consistent with the literature reports.

Compound 1b:

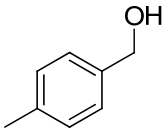


1b

^{1}H-NMR (ppm): 7.38 (m, 5H), 7.30 (m, 1H), 4.70 (s, 2H), 1.62 (br, 1H).

^{13}C-NMR (ppm): 140.8, 128.5, 127.7, 127.0, 65.3.

Compound 2b:

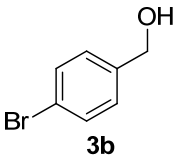


2b

^{1}H-NMR (ppm): 7.27 (m, 2H), 7.18 (m, 2H), 4.65 (s, 2H), 2.36 (s, 3H), 1.63 (br, 1H).

^{13}C-NMR (ppm): 137.9, 137.4, 129.3, 127.2, 65.2, 21.1.

Compound 3b:

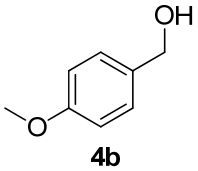


3b

^{1}H-NMR (ppm): 7.48 (m, 2H) 7.23 (m, 2H), 4.64 (s, 2H), 1.86 (br, 1H).

^{13}C-NMR (ppm): 139.7, 131.7, 128.6, 121.4, 64.5.

Compound 4b:

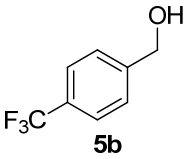


4b

^{1}H-NMR (ppm): 7.29 (m, 2H), 6.89 (m, 2H), 4.63 (s, 2H), 3.81 (s, 3H), 1.59 (br, 1H).

^{13}C-NMR (ppm): 133.1, 129.4, 128.5, 113.9, 65.1, 55.3.

Compound 5b:

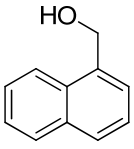


5b

^{1}H-NMR (ppm): 7.62(d, J=8.19Hz, 2H); 7.50 (d, J=8.19Hz, 2H); 4.78(s, 2H), 1.67 (br, 1H).

^{13}C-NMR (ppm): 144.6, 130.5, 126.8, 125.4(q, $J_{F\text{-}C}$=4.02Hz), 122.3, 64.5.

Compound 6b:

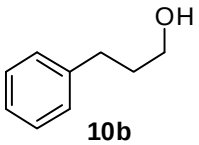


6b

^{1}H-NMR (ppm): 8.07 (m, 1H), 7.89 (m, 1H), 7.80 (m, 1H), 7.53 (m, 2H), 7.46 (m, 2H), 5.06(s, 2H), 2.49 (br, 1H).

^{13}C-NMR (ppm): 136.3, 133.7, 131.2, 128.6, 128.5, 126.3, 125.8, 125.4, 125.3, 123.6, 63.4.

Compound 10b:

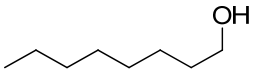


10b

^{1}H-NMR (ppm): 7.29 (m, 2H), 7.20 (m, 3H), 3.68 (t, J=6.44Hz, 2H), 2.72 (t, J=6.41 Hz, 2H), 1.90 (m, 2H), 1.64 (br, 1H).

^{13}C-NMR (ppm): 141.8, 128.4 (2 peaks), 125.9, 62.3, 34.2, 32.1.

Compound 11b:

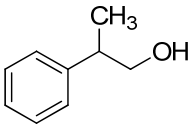


11b

^{1}H-NMR (ppm): 3.64 (t, J=6.73Hz, 2H), 1.55 (q, J=6.73Hz, 2H), 1.49 (br, 1H), 1.41-1.20 (m, 10H), 0.88 (m, 3H).

^{13}C-NMR (ppm): 63.1, 32.8, 31.8, 29.3 (2 peaks), 25.6, 22.7, 14.1.

Compound 14b:

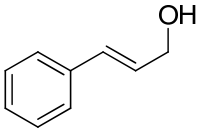


14b

^{1}H-NMR (ppm): 7.34-7.23 (m, 5H), 3.70 (m, 2H), 2.95 (m, 1H), 1.61 (br, 1H), 1.28 (d, J=7.03Hz, 3H).

^{13}C-NMR (ppm): 143.7, 128.6, 127.5, 126.7, 68.7, 42.4, 17.6.

Compound 15b:

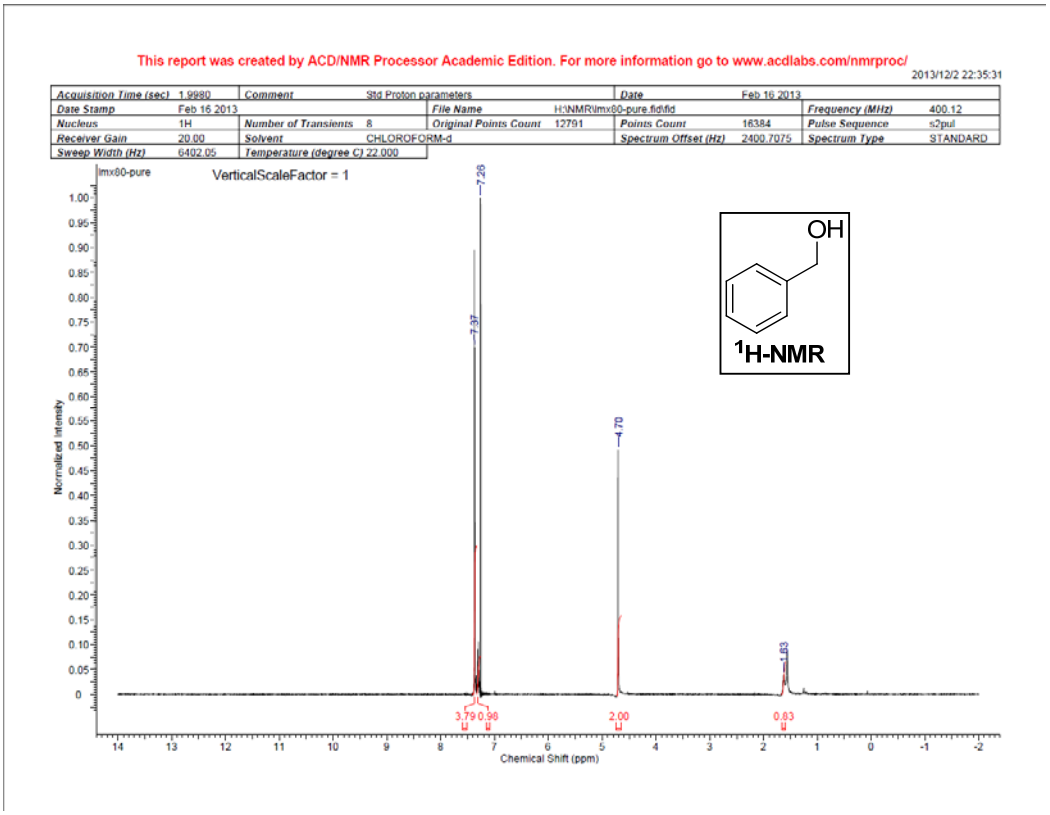


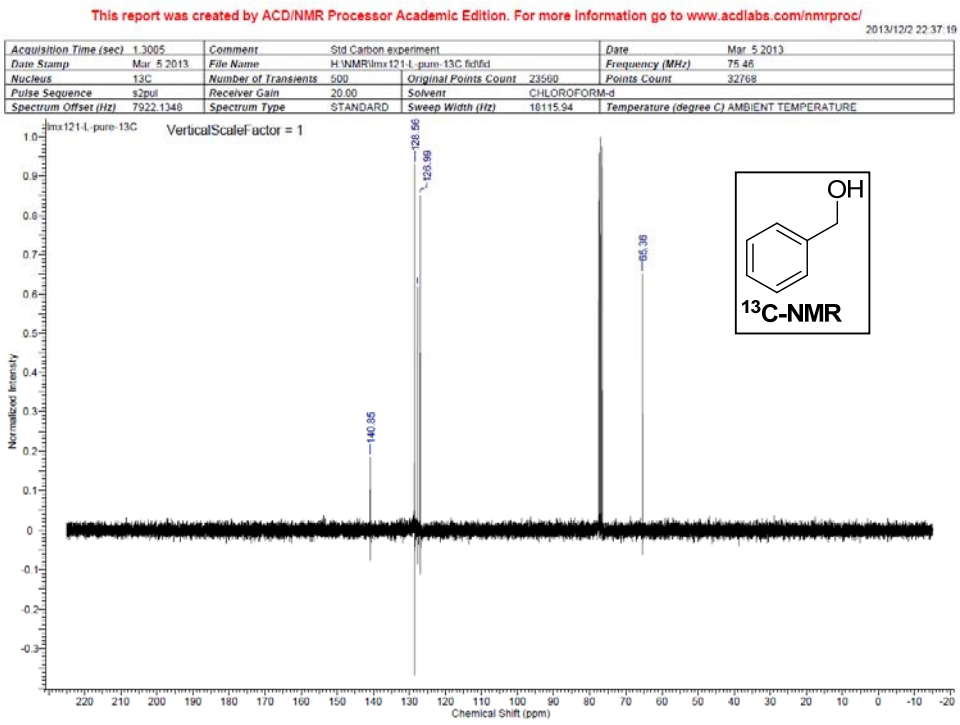
15b

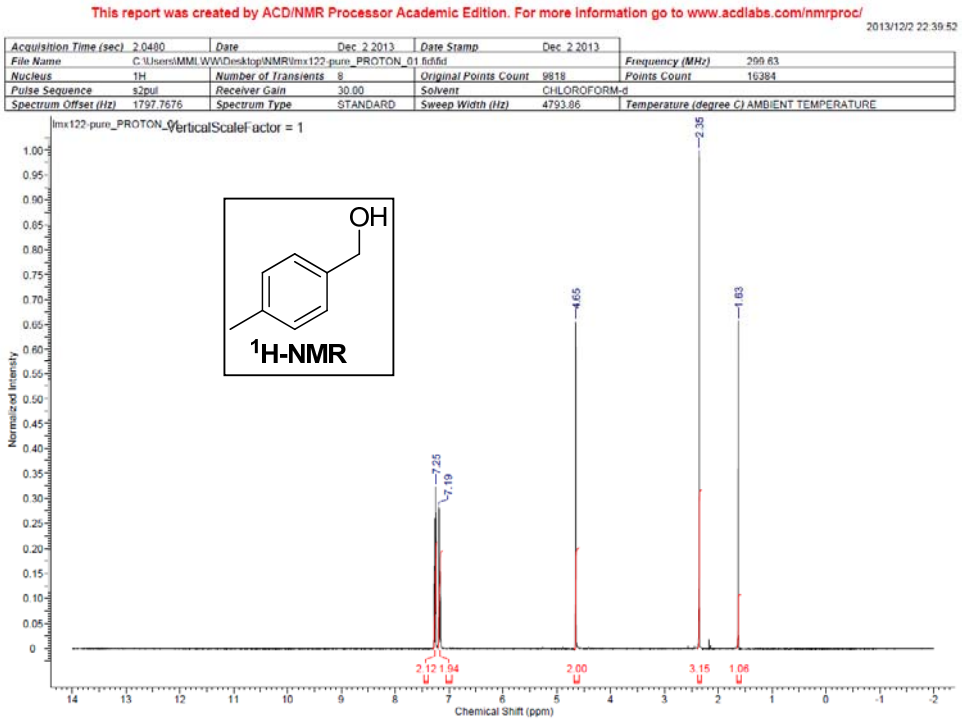
^{1}H-NMR (ppm): 7.43-7.19 (m, 5H), 6.62 (d, J=16.09Hz, 1H), 6.36 (dt, J= 16.09, 5.56Hz, 1H), 4.32 (d, J=5.56 Hz, 2H), 1.72 (br, 1H).

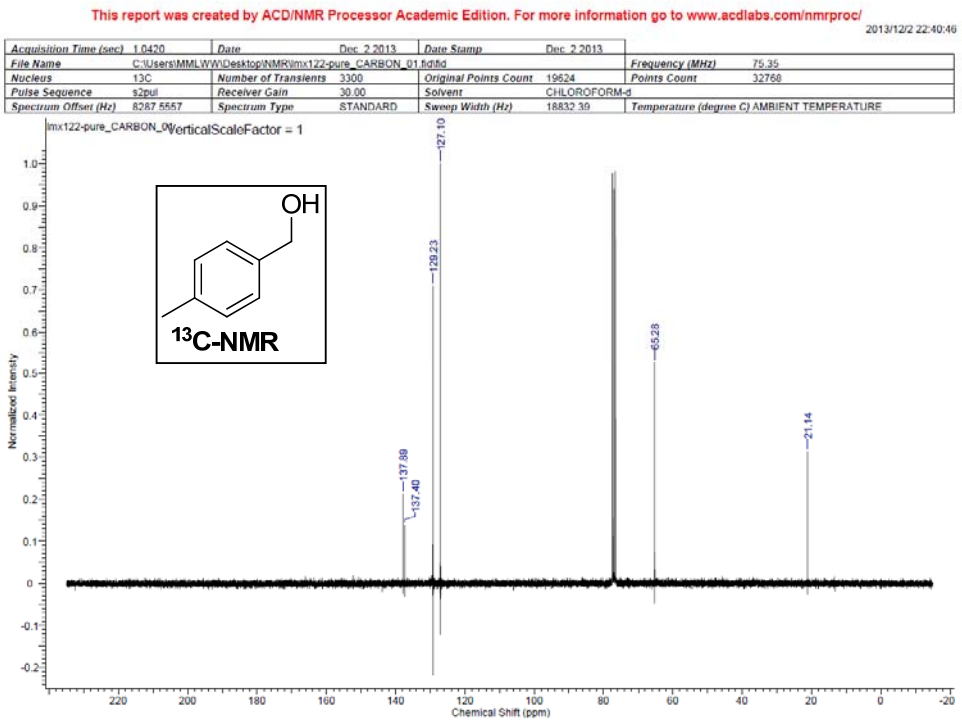
^{13}C-NMR (ppm): 136.6, 131.1, 128.6, 127.7, 126.4, 63.7.

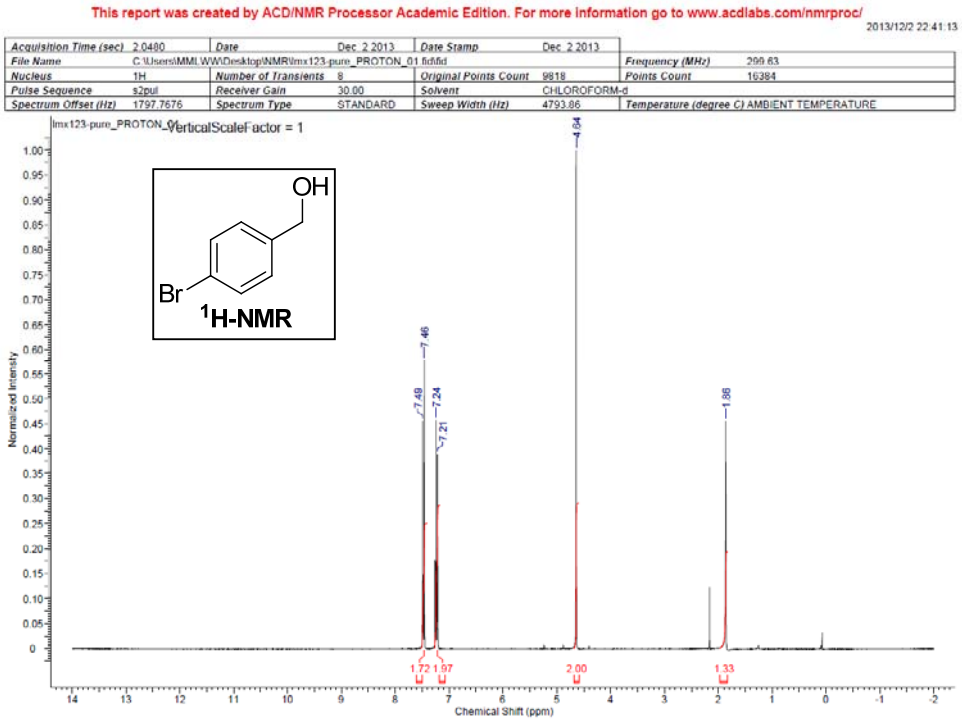
V. NMR Datas







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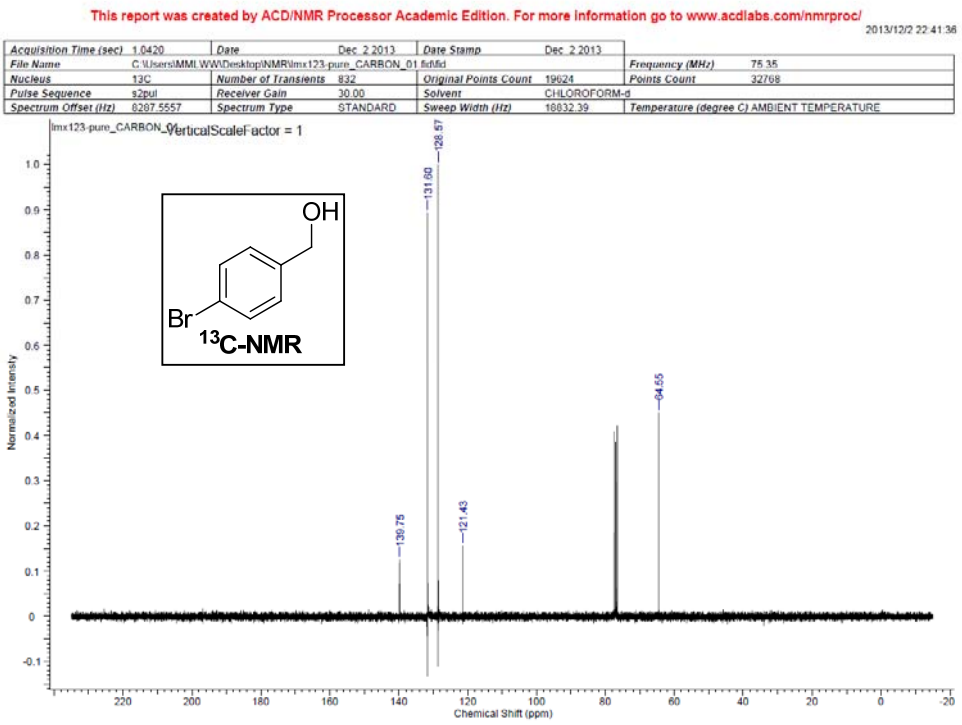
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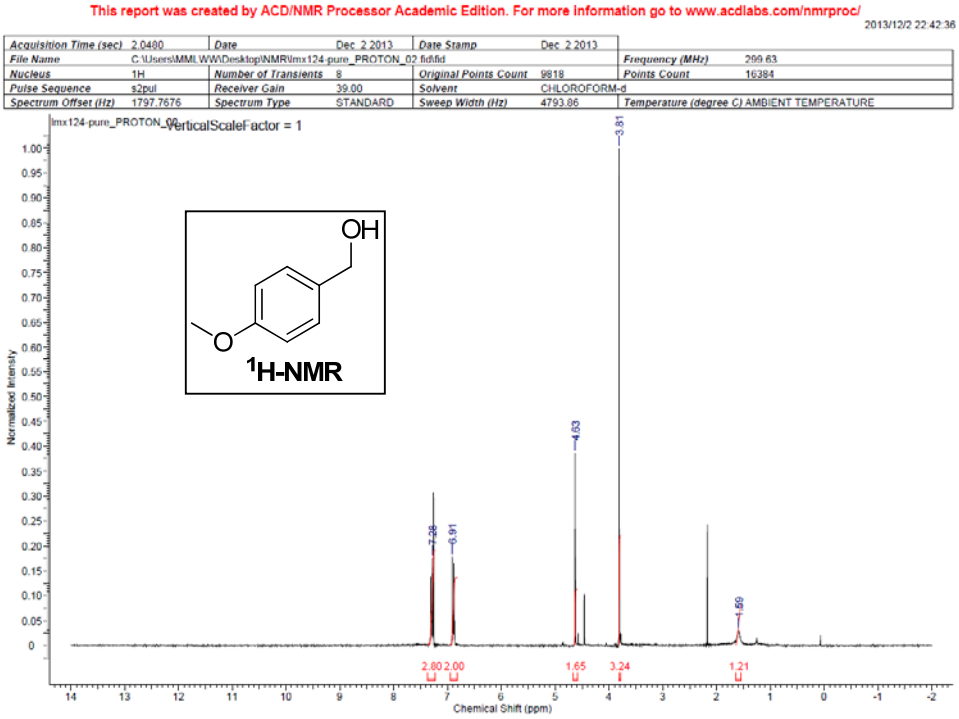

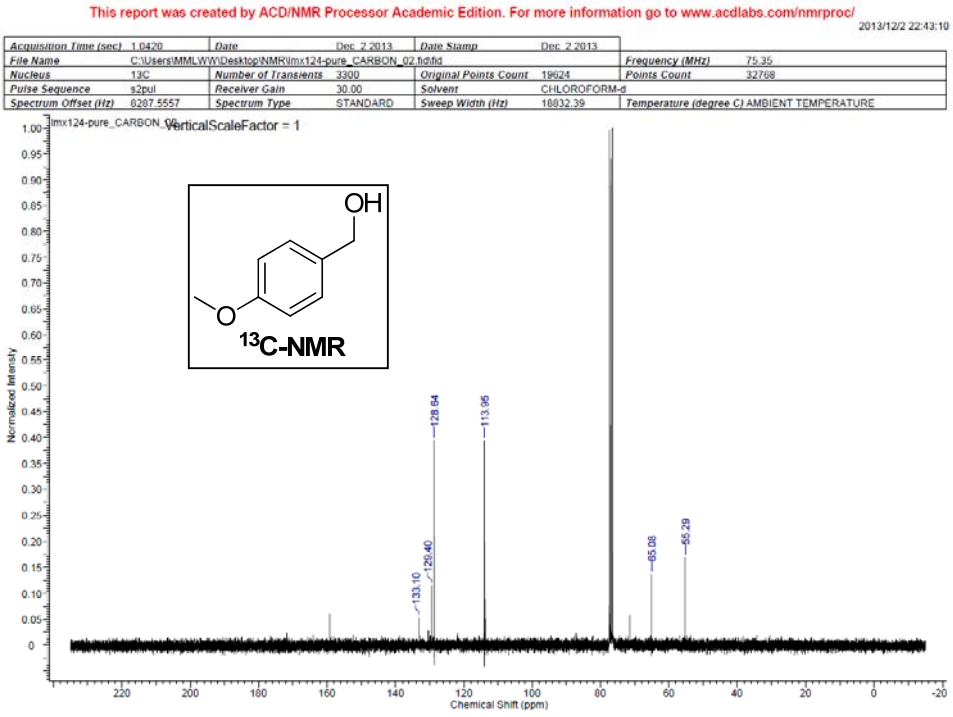

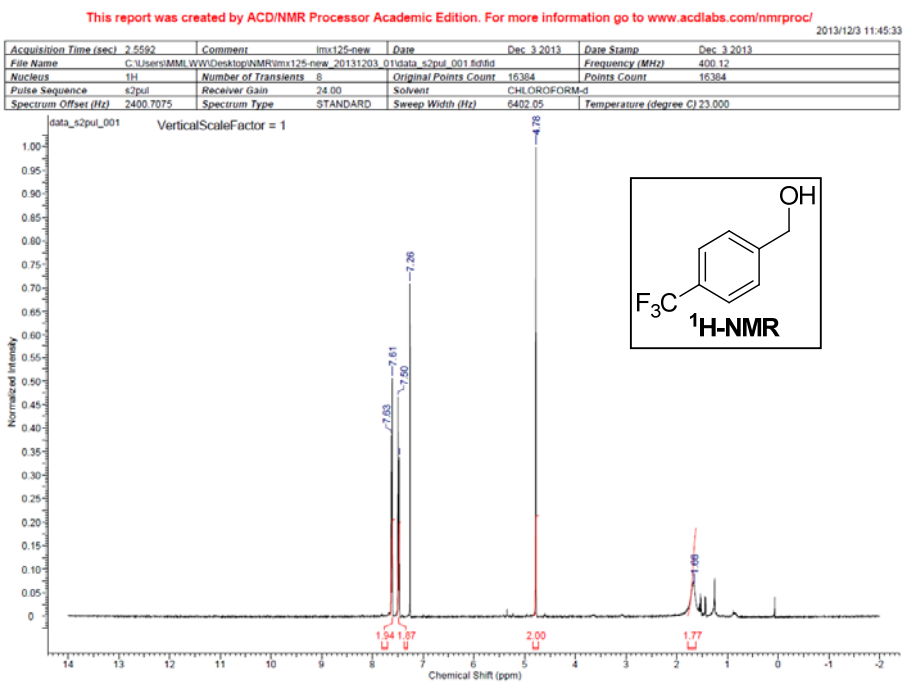

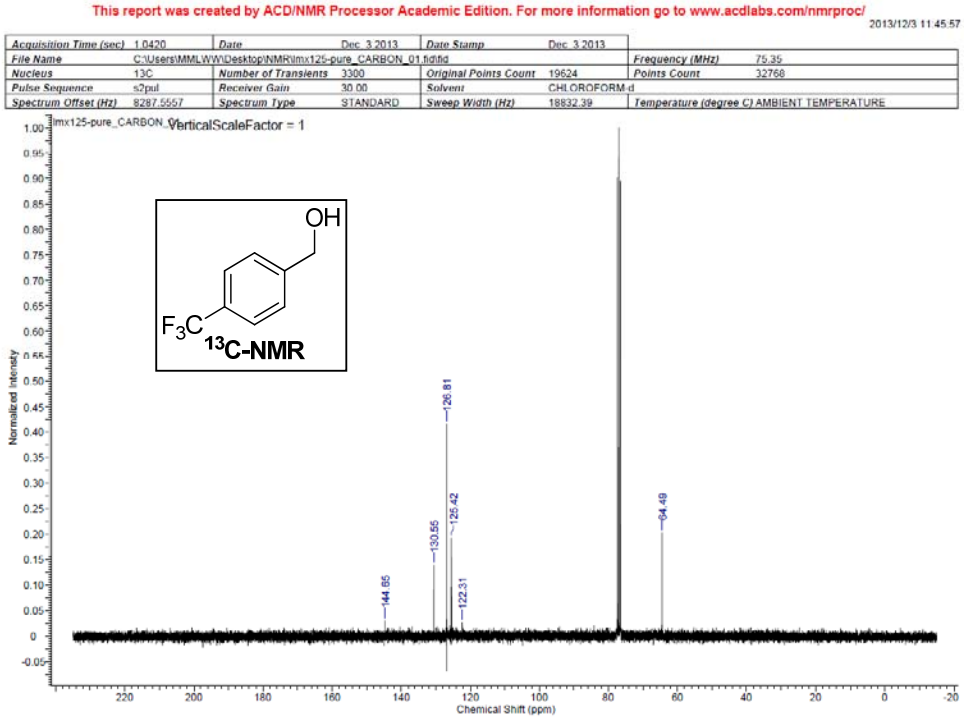

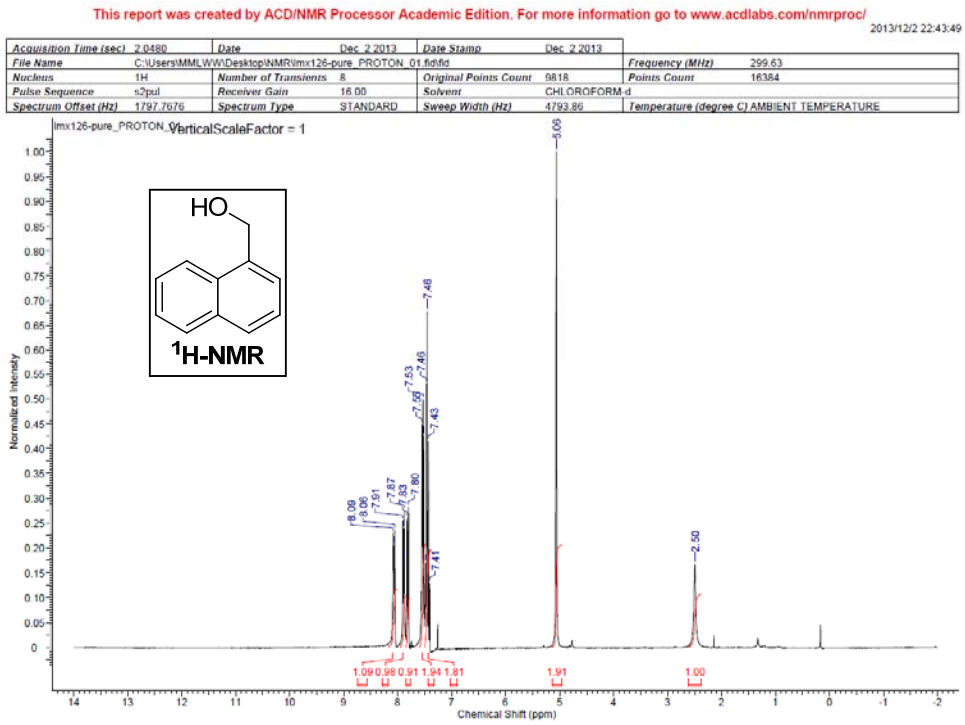

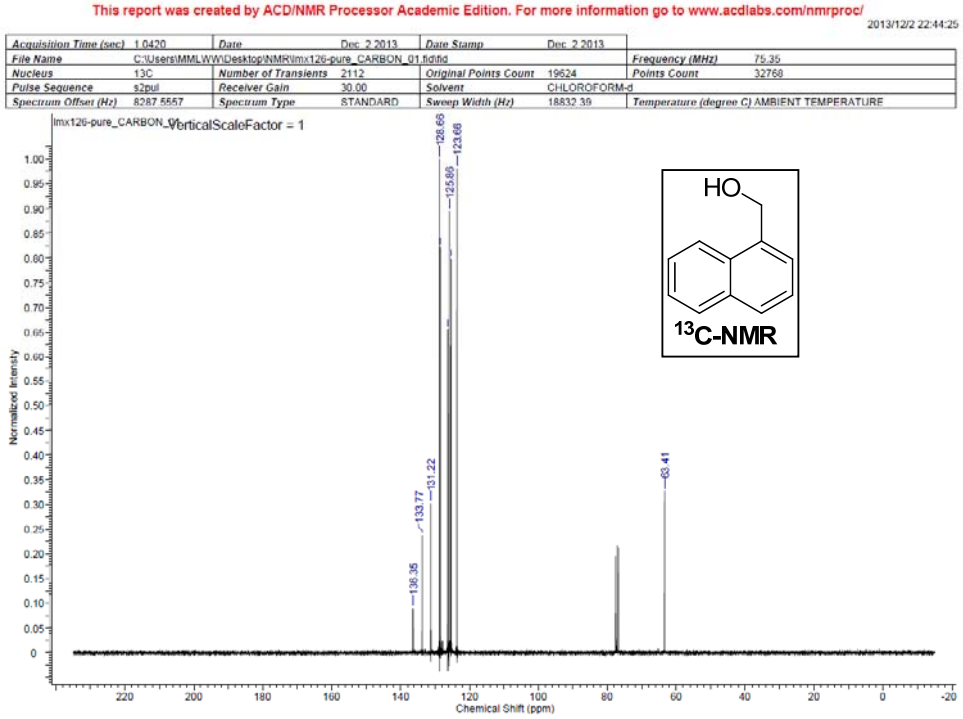
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Normalized Intensity
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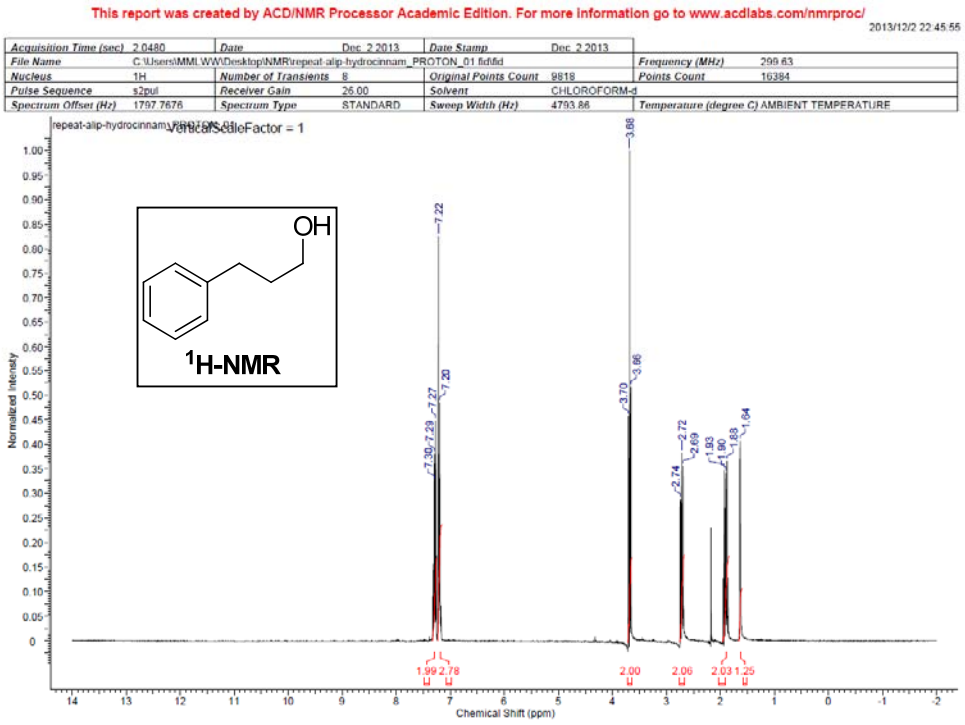
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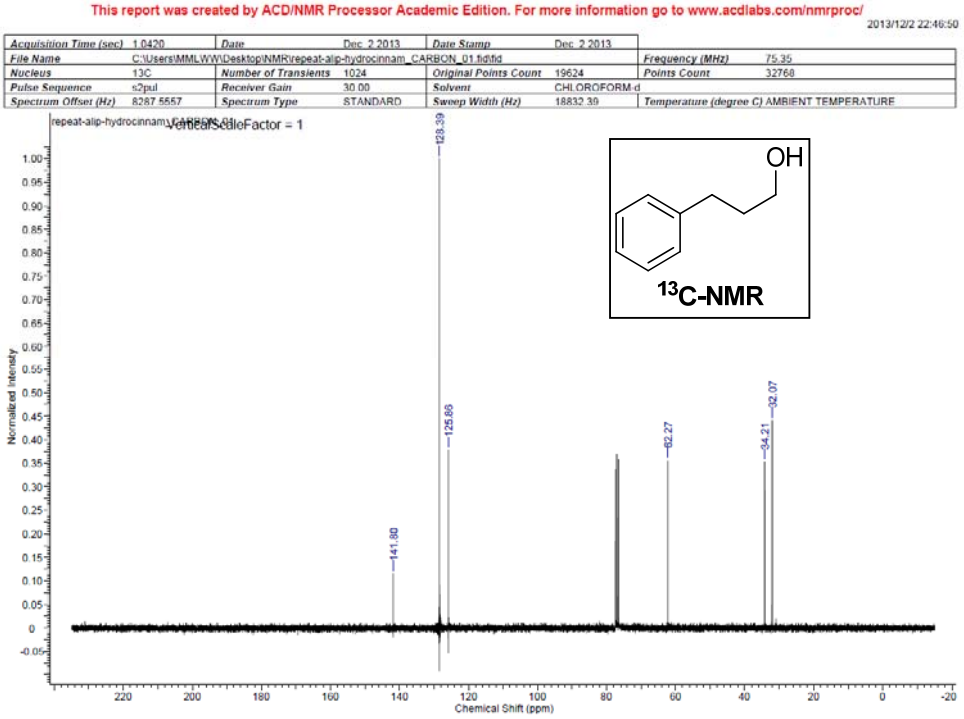
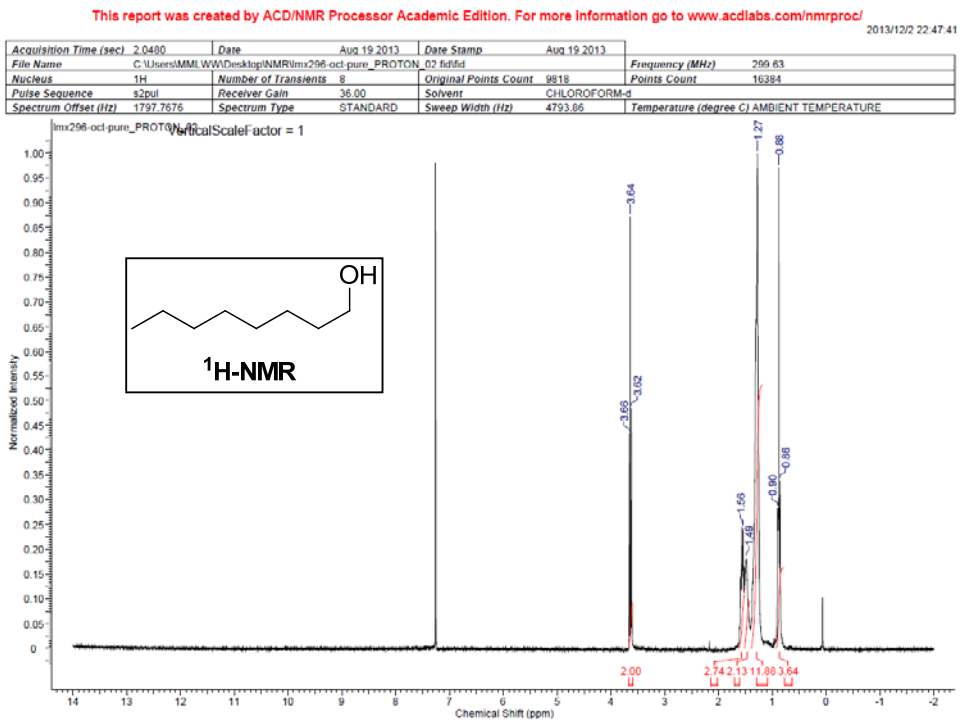
Sweep Width (Hz) 4793.86
Temperature (degree C) AMBIENT TEMPERATURE
repeat-allp-hydrocinnam_PROTON_01
VerticalScaleFactor = 1
7.22
7.27
7.29
7.30
7.20
3.68
3.70
3.66
2.74
2.72
2.69
1.93
1.90
1.83
1.64
OH
1H-NMR
1.99
2.78
2.00
2.06
2.03
1.25
Normalized Intensity
Chemical Shift (ppm)


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
2013/12/2 22:46:50
Acquisition Time (sec) 1.0420
Date Dec 2 2013
Date Stamp Dec 2 2013
File Name C:\Users\MMLWW\Desktop\NMR\repeat-alip-hydrocinnam_CARBON_01.fid\fid
Frequency (MHz) 75.35
Nucleus 13C
Number of Transients 1024
Original Points Count 19624
Points Count 32768
Pulse Sequence s2pul
Receiver Gain 30.00
Solvent CHLOROFORM-d
Spectrum Offset (Hz) 8287.5557
Spectrum Type STANDARD
Sweep Width (Hz) 18832.39
Temperature (degree C) AMBIENT TEMPERATURE
VerticalScaleFactor = 1
128.39
125.88
62.27
34.21
32.07
141.80
OH
13C-NMR
Normalized Intensity
Chemical Shift (ppm)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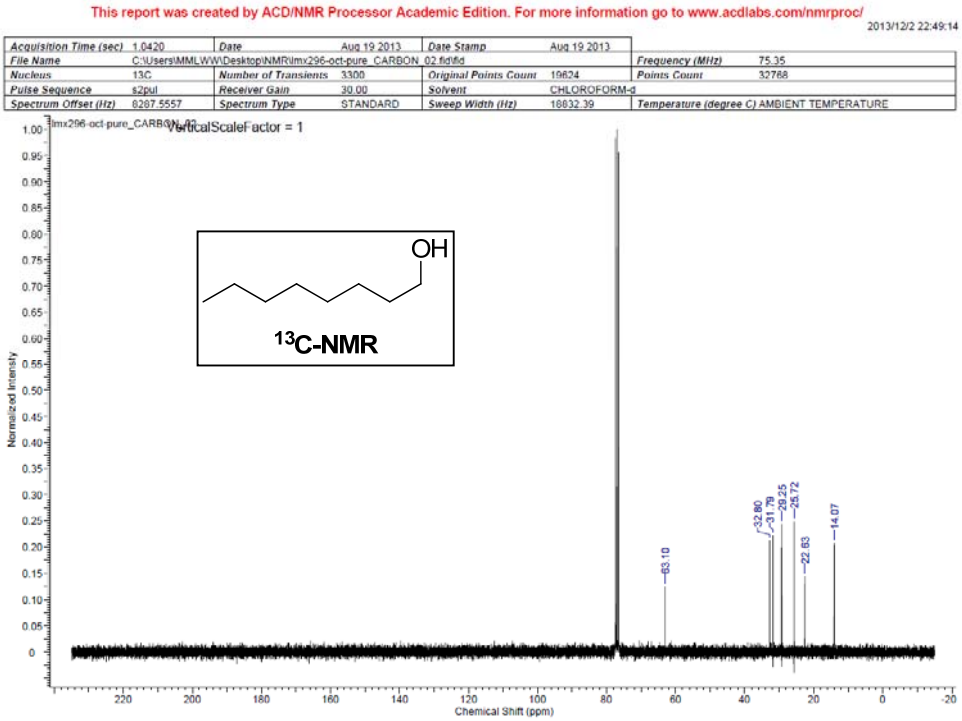
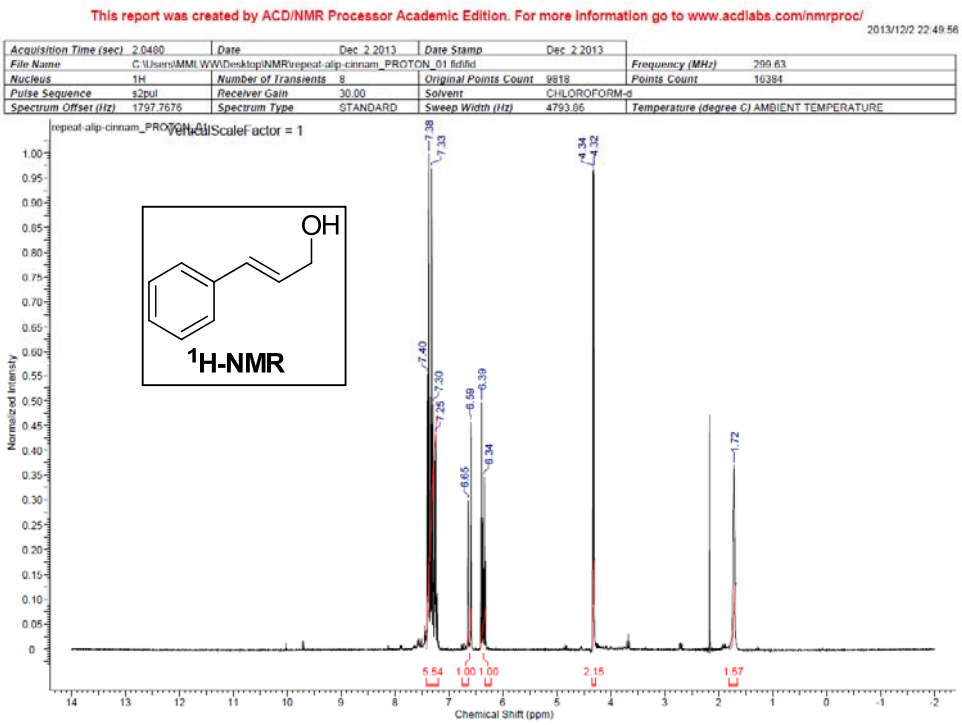
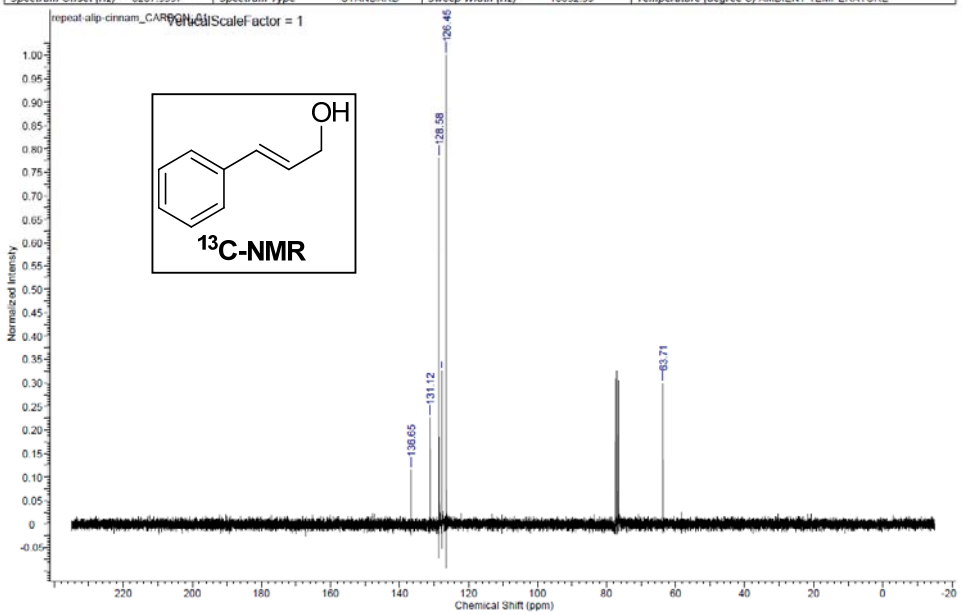
2013/12/2 22:47:41
Acquisition Time (sec) 2.0480
Date Aug 19 2013
Date Stamp Aug 19 2013
File Name C:\Users\MMLWW\Desktop\NMR\lmx296-oct-pure_PROTON_02.fid\fid
Frequency (MHz) 299.63
Nucleus 1H
Number of Transients 8
Original Points Count 9818
Points Count 16384
Pulse Sequence s2pul
Receiver Gain 36.00
Solvent CHLOROFORM-d
Spectrum Offset (Hz) 1797.7676
Spectrum Type STANDARD
Sweep Width (Hz) 4793.66
Temperature (degree C) AMBIENT TEMPERATURE
VerticalScaleFactor = 1
3.64
3.66
3.62
1.27
0.88
1.58
1.49
0.90
0.88
2.00
2.74
2.13
11.88
3.64
OH
1H-NMR
Normalized Intensity
Chemical Shift (ppm)


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
2013/12/2 22:49:14
VerticalScaleFactor = 1
OH
13C-NMR
Normalized Intensity
Chemical Shift (ppm)
63.10
32.80
31.79
31.35
25.72
22.83
14.07


This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/
2013/12/2 22:49:56
VerticalScaleFactor = 1
OH
1H-NMR
Normalized Intensity
Chemical Shift (ppm)
7.38
7.33
4.34
4.32
7.40
7.30
7.25
6.59
6.39
6.34
6.65
1.72
5.54
1.00
1.00
2.15
1.57

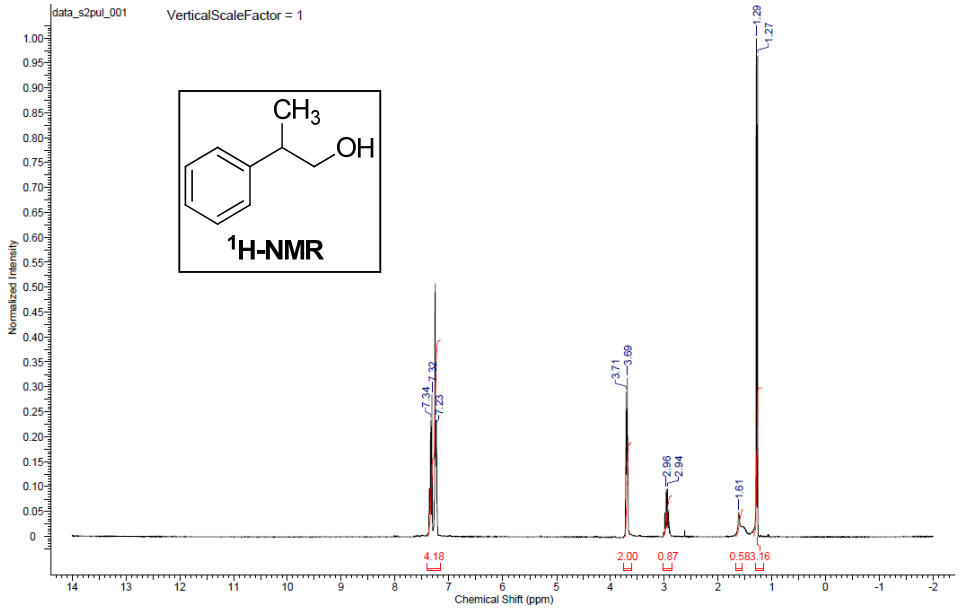
2013/12/2 22:50:19

Acquisition Time (sec)	1.0420	Date	Dec 2 2013	Date Stamp	Dec 2 2013		
File Name	C:\Users\MMLWW\Desktop\NMR\repeat-alip-cinnam_CARBON_01.fid\fid					Frequency (MHz)	75.35
Nucleus	13C	Number of Transients	320	Original Points Count	19624	Points Count	32768
Pulse Sequence	s2pul	Receiver Gain	30.00	Solvent	CHLOROFORM-d		
Spectrum Offset (Hz)	8287.5557	Spectrum Type	STANDARD	Sweep Width (Hz)	18832.39	Temperature (degree C)	AMBIENT TEMPERATURE



2014/1/6 18:32:51

Acquisition Time (sec)	2.0480	Comment	add-alip-phenylpropionaldehyde-final			Date	Jan 3 2014
Date Stamp	Jan 3 2014	File Name	C:\Users\MMLWW\Desktop\add-alip-phenylpropionaldehyde-final_20140103_01\data_s2pul_001.fid\fid				
Frequency (MHz)	300.06	Nucleus	1H	Number of Transients	8	Original Points Count	9832
Points Count	16384	Pulse Sequence	s2pul	Receiver Gain	24.00	Solvent	CHLOROFORM-d
Spectrum Offset (Hz)	1800.3330	Spectrum Type	STANDARD	Sweep Width (Hz)	4800.77	Temperature (degree C)	25.000



2014/1/6 18:27:17

Acquisition Time (sec)	1.0420	*Comment*	add-alip-phenylpropionaldehyde-final			*Date*	Jan 3 2014
Date Stamp	Jan 3 2014						
File Name	C:\Users\MMLWW\Desktop\add-alip-phenylpropionaldehyde-final_20140103_02\add-alip-phenylpropionaldehyde-final_CARBON_2_20140103_02.fid\fid						
Frequency (MHz)	75.46	*Nucleus*	13C	*Number of Transients*	1651	*Original Points Count*	19661
Points Count	32768	*Pulse Sequence*	s2pul	*Receiver Gain*	30.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	8299.3770	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	18867.92	*Temperature (degree C)*	25.000