

Separation of Alkyne Enantiomers by Chiral Column HPLC Analysis of Their Cobalt-Complexes

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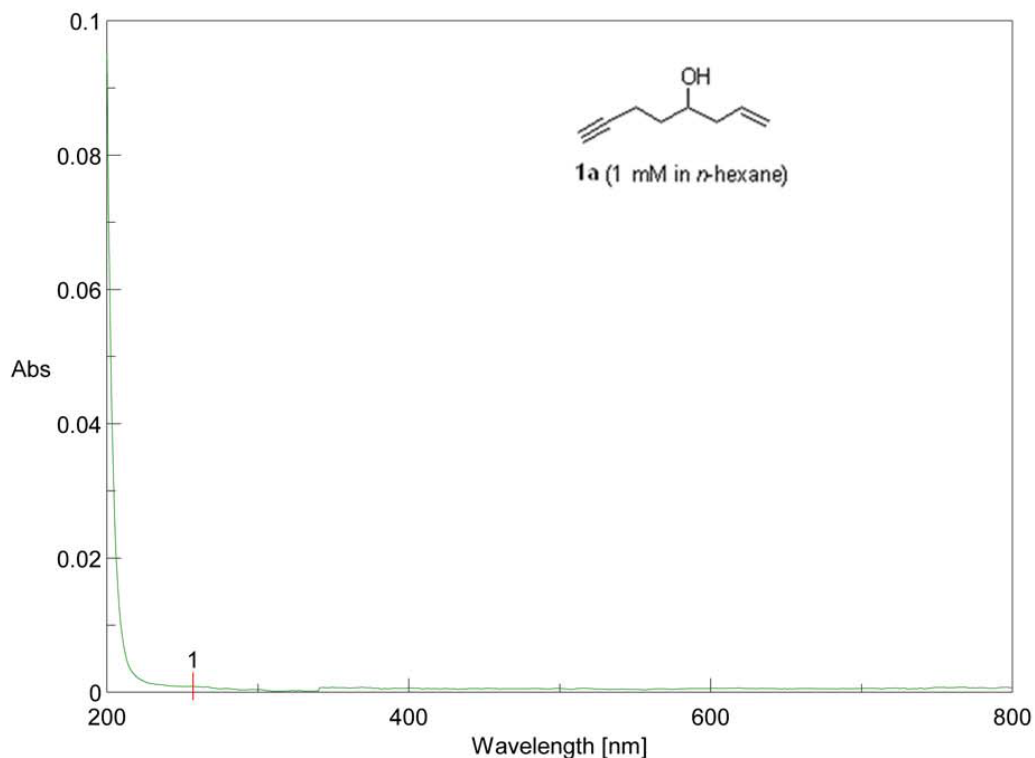
1. General Information

Reagents were used as received from commercial suppliers unless otherwise indicated. All reactions were carried out under an atmosphere of Ar unless otherwise indicated. Column chromatography was performed with silica gel 60 (160-200 mesh, Qingdao Haiyang Chemical Factory). Analytical thin-layer chromatography (TLC) was performed with glass TLC plates (Qingdao silica gel GF-F₂₅₄ plates). Visualization was accomplished with UV light, or potassium permanganate staining, or phosphomolybdic acid staining and subsequent heating.

UV-Vis spectra were acquired on JASCO-V750 Spectrophotometer. HPLC analysis were acquired on SHIMAZU SCL-10Avp. The CHIRALPAK-IB column is analytical type with the packing composition of cellulose tris(3,5-dimethylphenylcarbamate), internal diameter of 4.6 mm, column length of 250 mm, and particle size of 5 μ m. The CHIRALPAK-IA column is analytical type with the packing composition of amylose tris(3,5-dimethylphenylcarbamate), internal diameter of 4.6 mm, column length of 250 mm, and particle size of 5 μ m. ¹H-, and ¹³C-NMR spectra were acquired on Mercury-300, or Bruker AVANCE III-400, or WNMRI-500, or VNMR-600 spectrometers. Chemical shifts are indicated in parts per million (ppm) downfield from tetramethylsilane (TMS, δ = 0.00) with residual undeuterated solvent peaks as internal reference for ¹H-NMR and deuterated solvent peaks shifts for ¹³C-NMR. Multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or combinations of those. For NMR analysis of the Co₂(CO)₈-alkyne complexes, the sample solution in CDCl₃ should pass through a disposable syringe filter (Nylon 66, 0.22 μ m, 13 mm) immediately before the NMR experiment, to remove the tiny amount of paramagnetic material. Mass spectra are electron ionization (EI) or electrospray ionization (ESI). EI-MS data were measured on Micromass GCT mass spectrometer. ESI-MS data were measured on Thermo Exactive Orbitrap plus spectrometer.

2. UV-Vis spectra of **1a** and **2a**

Peak Find - 1a-1mM.jws



[Detailed Information]

Creation date 2017/1/17 9:25
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 Horizontal axis Wavelength [nm]
 Vertical axis Abs
 Start 800 nm
 End 200 nm
 Data interval 1 nm
 Data points 601

[Measurement Information]

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 Model name V-750
 Serial No. A027961799
 Accessory USE-753
 Accessory S/N A027961799
 Cell
 Ref. beam

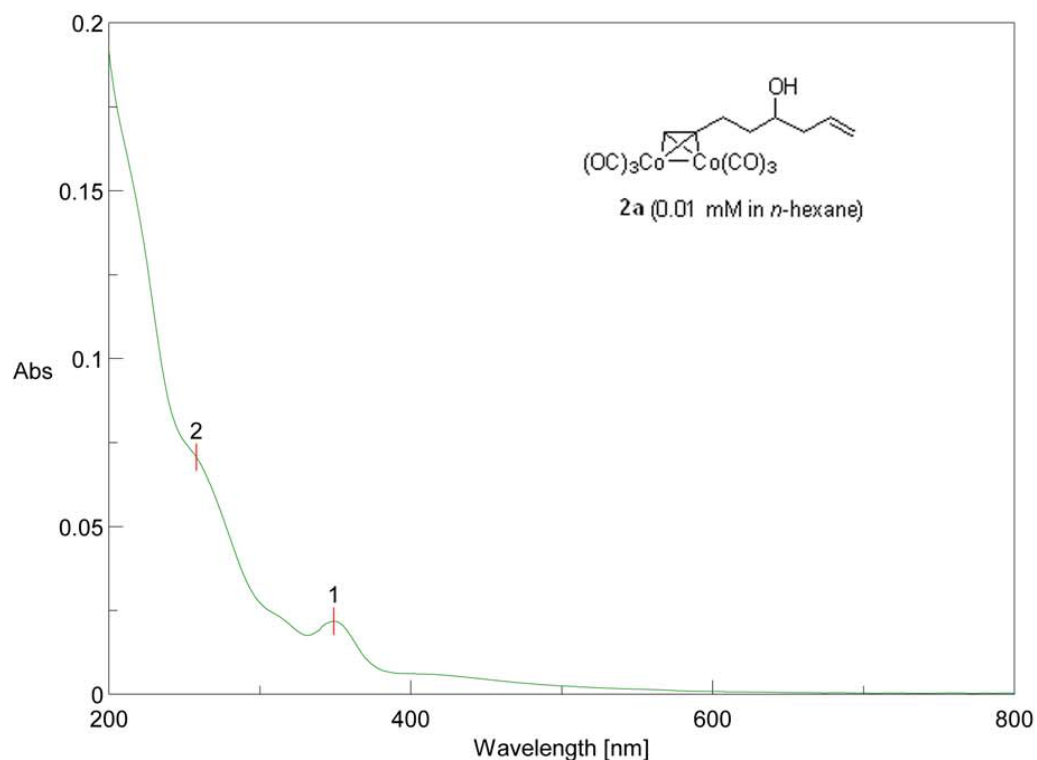
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 Response 0.24 sec
 Scan speed 2000 nm/min
 Change source at 340 nm
 Light source D2/WI
 Filter exchange Step
 Correction Baseline

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity
1	257	0.000860114			

Peak Find - 2a.jws



[Detailed Information]

Creation date 2017/1/13 16:50
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Horizontal axis Wavelength [nm]
Vertical axis Abs
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End 200 nm
Data interval 1 nm
Data points 601

[Measurement Information]

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Model name V-750
Serial No. A027961799
Accessory USE-753
Accessory S/N A027961799
Cell
Ref. beam
Measurement date 2017/1/13 16:49

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Bandwidth 2.0 nm
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Correction Baseline

[Result of Peak Picking]

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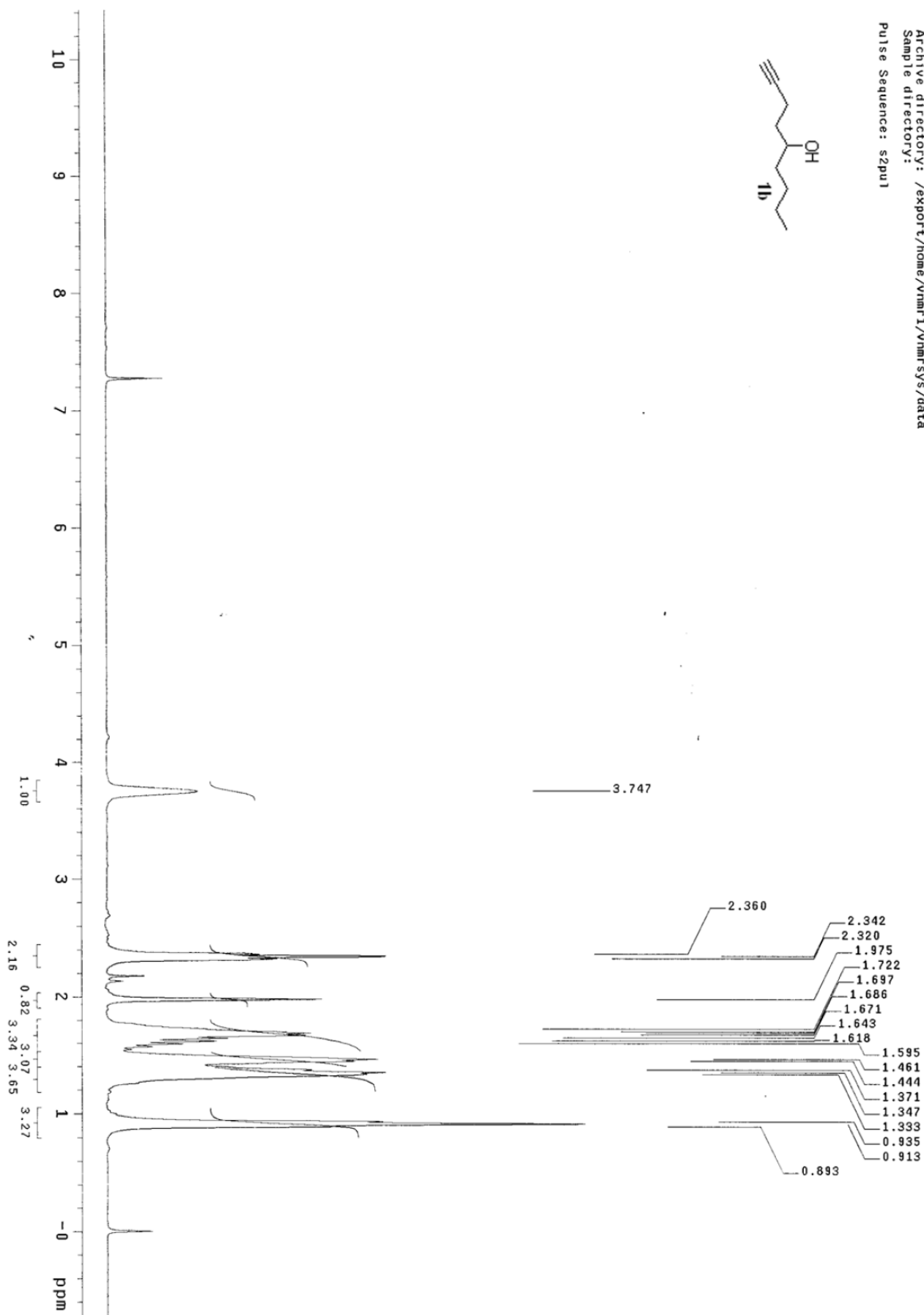
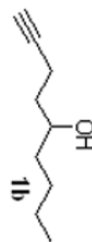
3. ^1H - and ^{13}C -NMR spectra of **1b**, and **1g-j**

1b-CDCl₃-300MHz

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Sample directory:

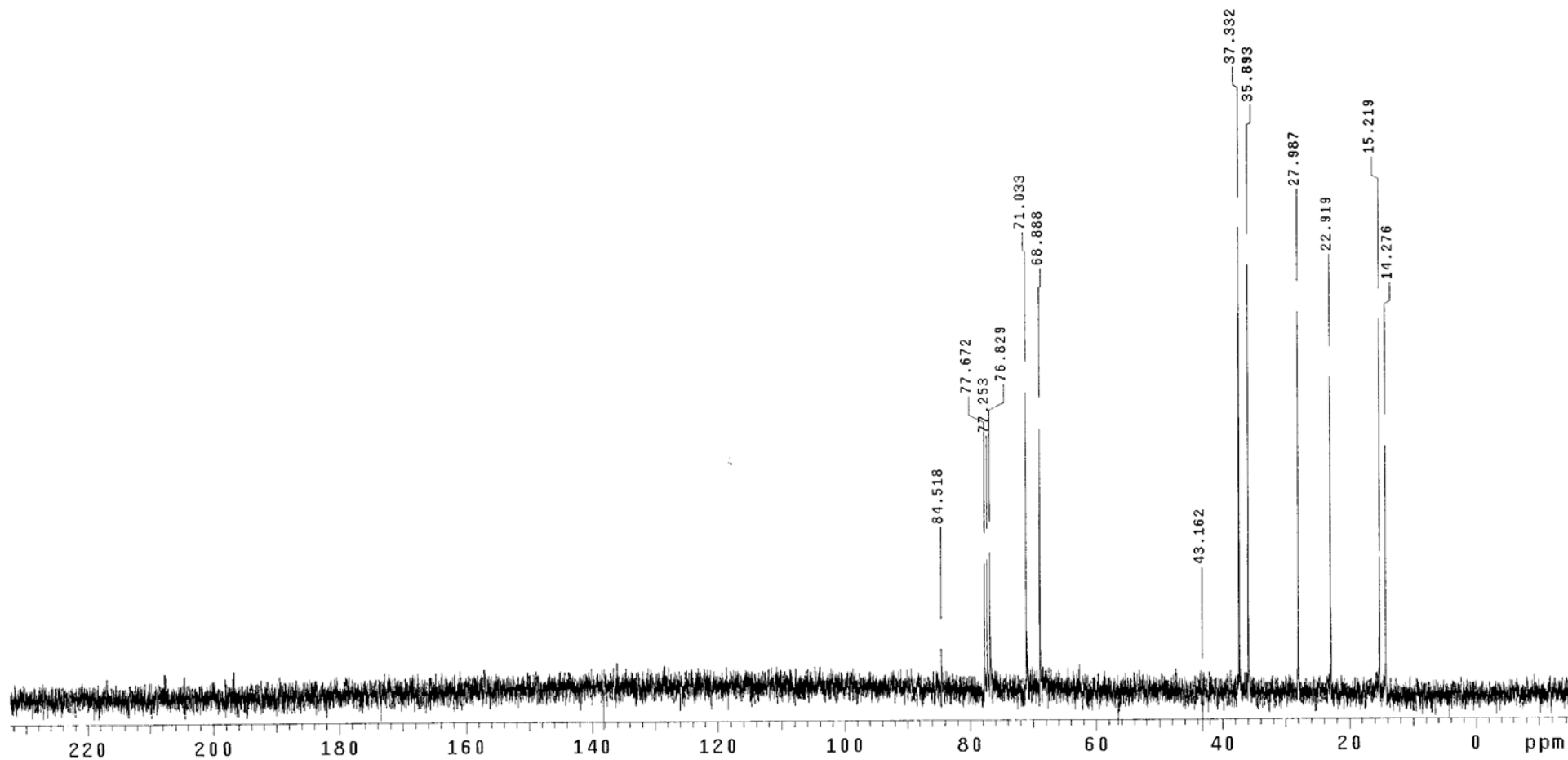
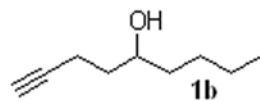
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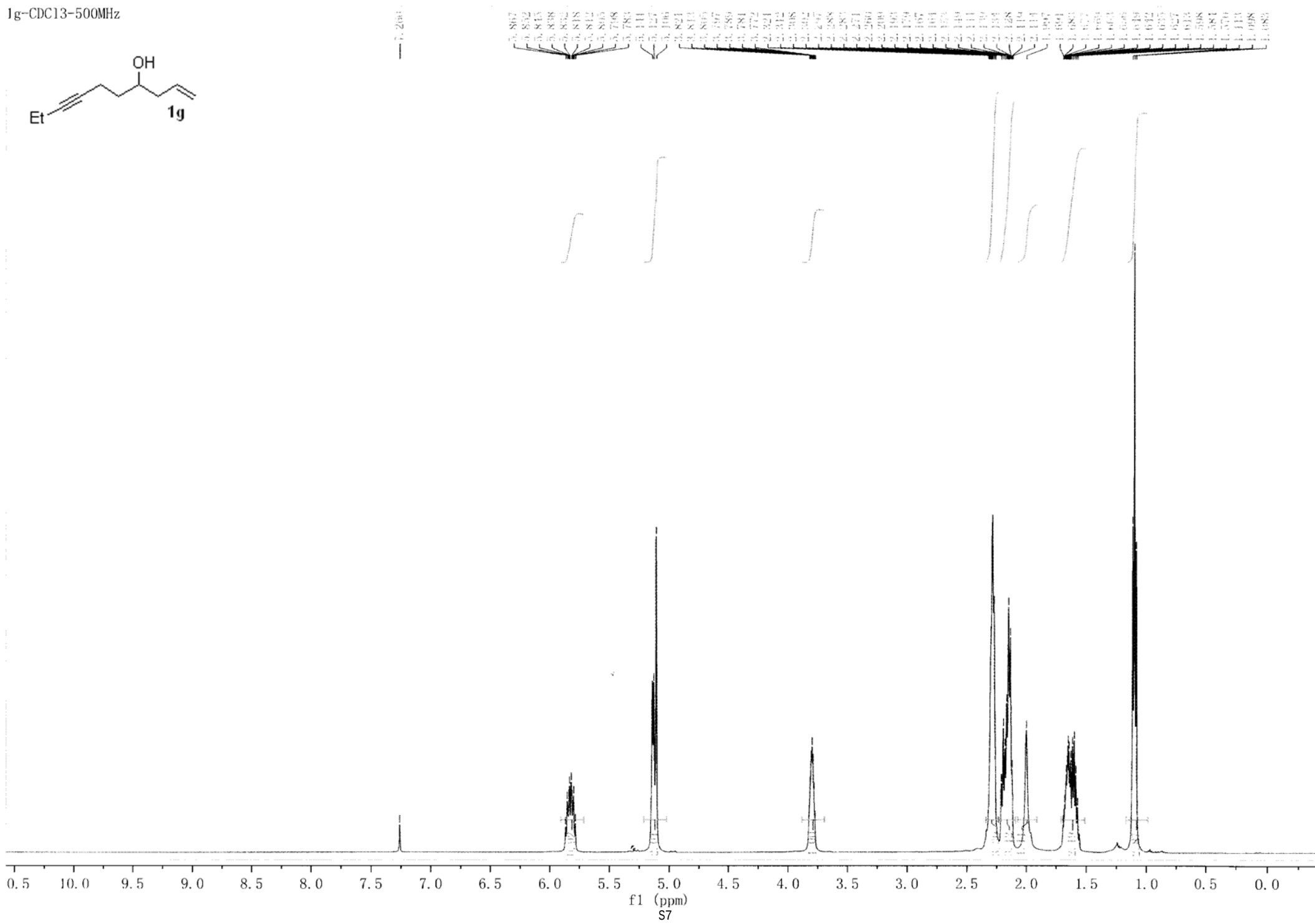
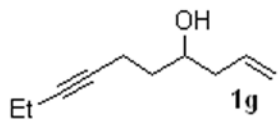
1b-CDC13-300MHz

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Sample directory:

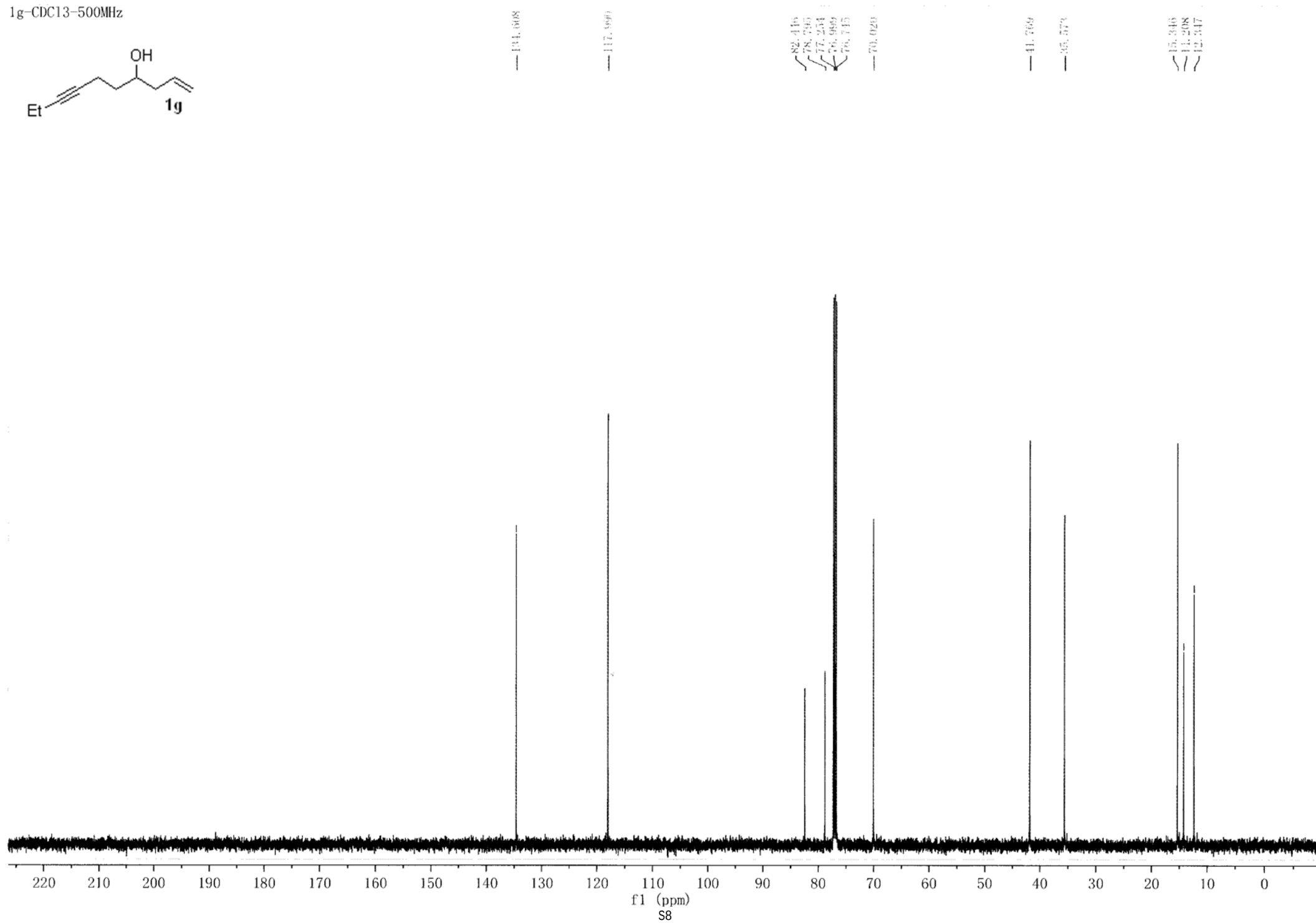
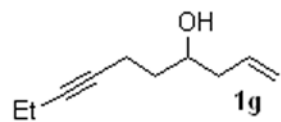
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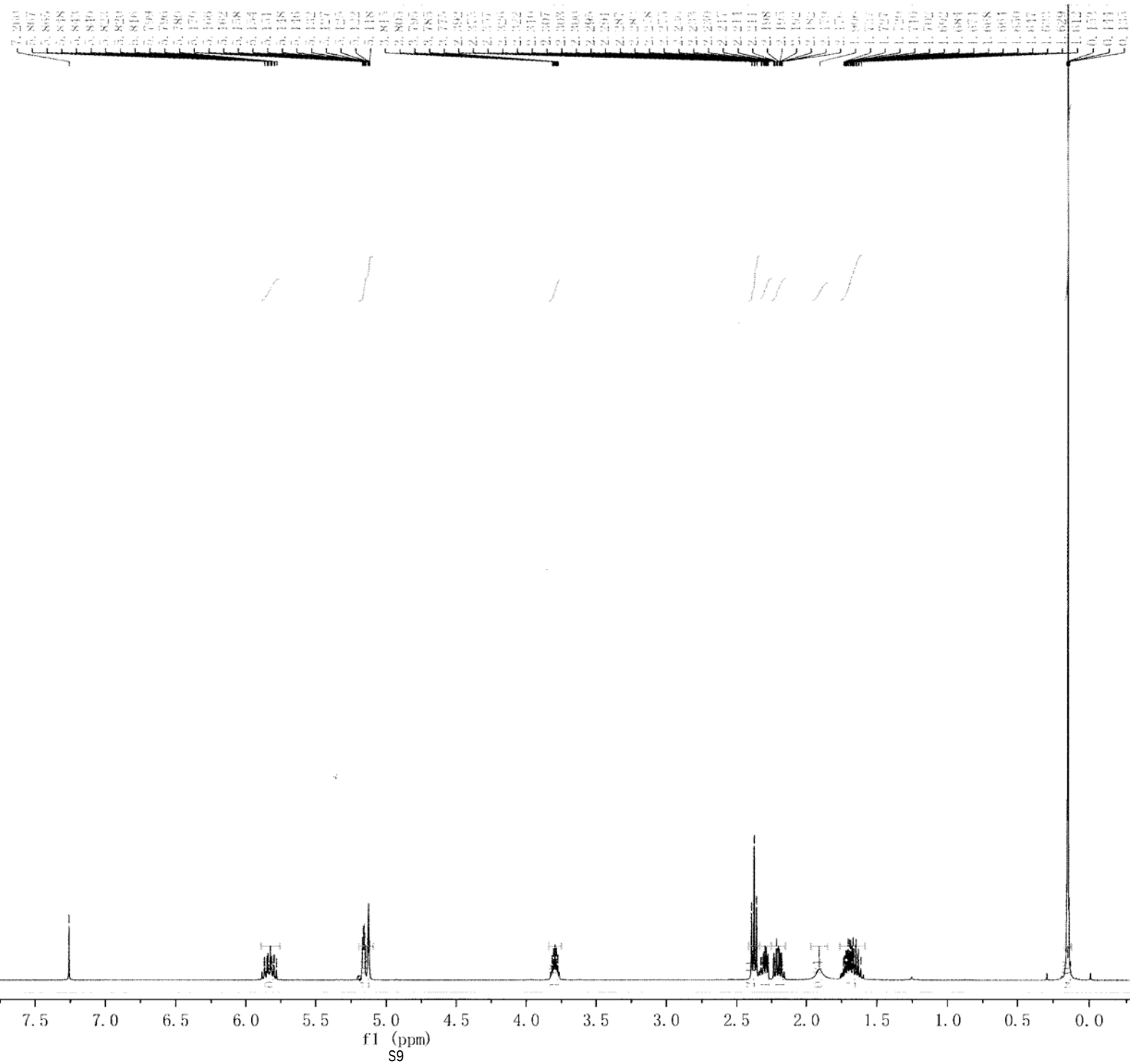
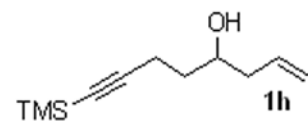
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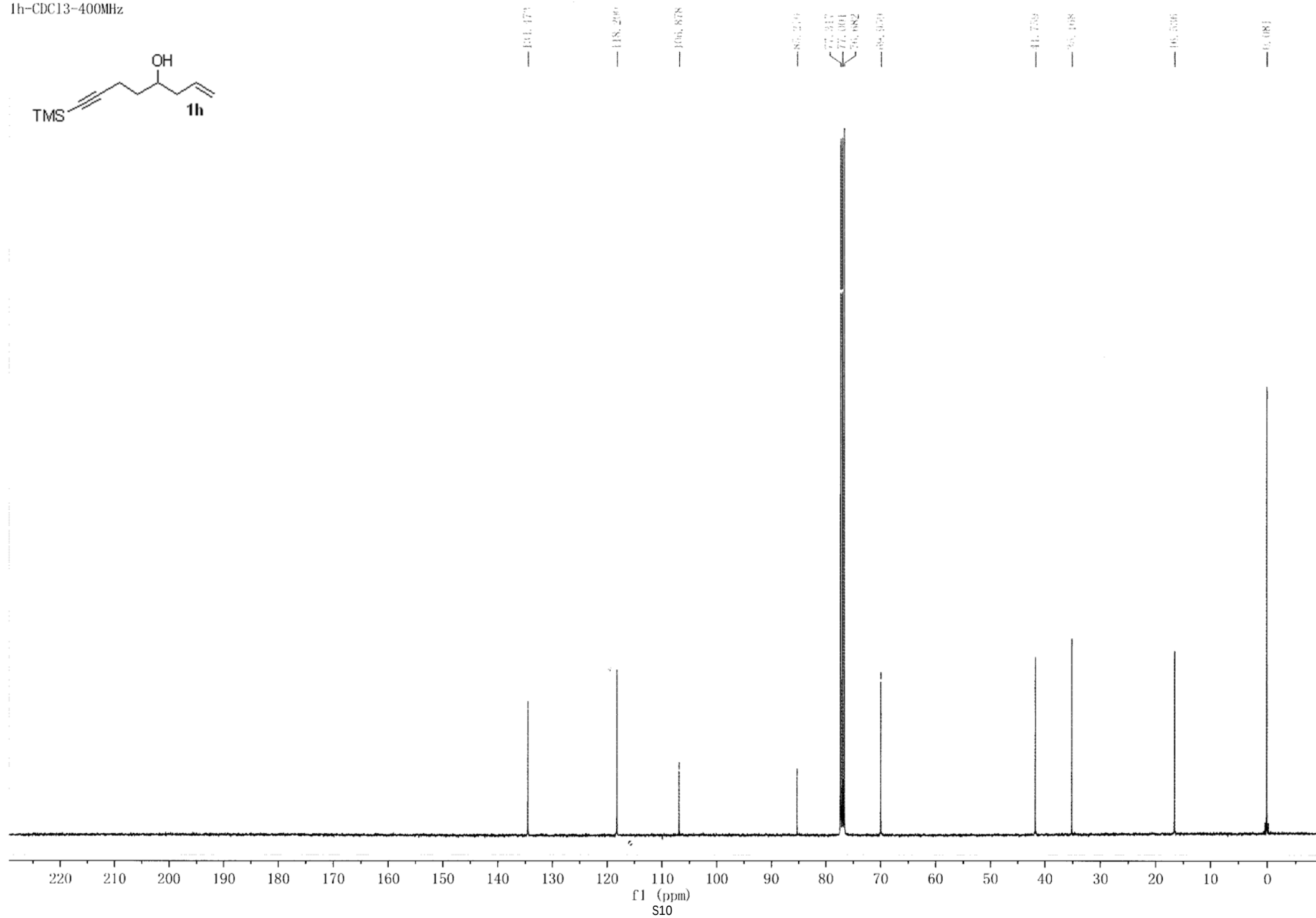
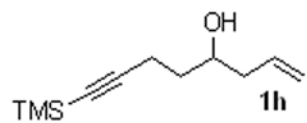
1g-CDC13-500MHz



1h-CDC13-400MHz



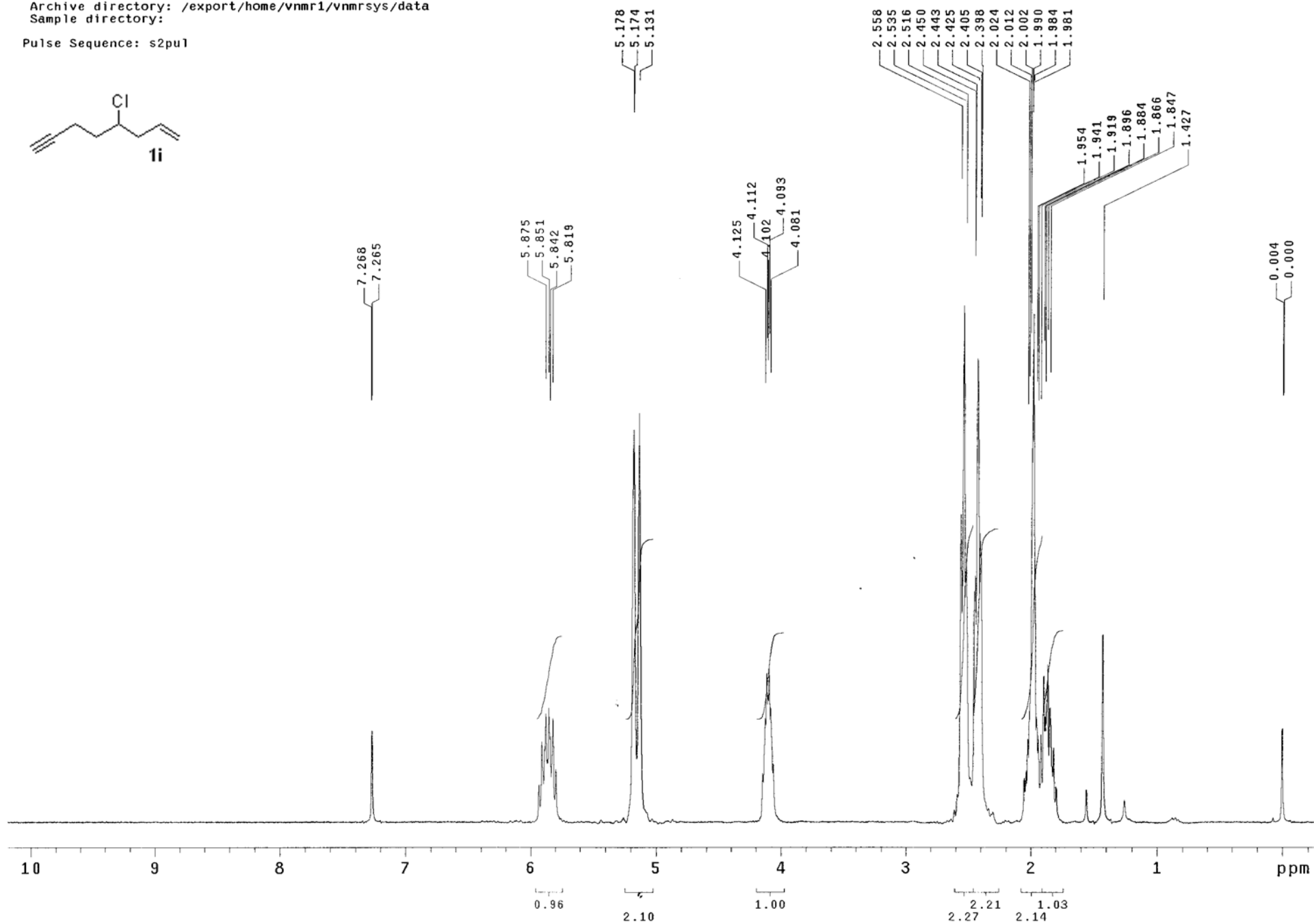
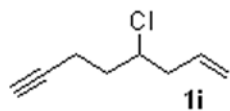
1h-CDC13-400MHz



1i-CDC13-300MHZ

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Sample directory:

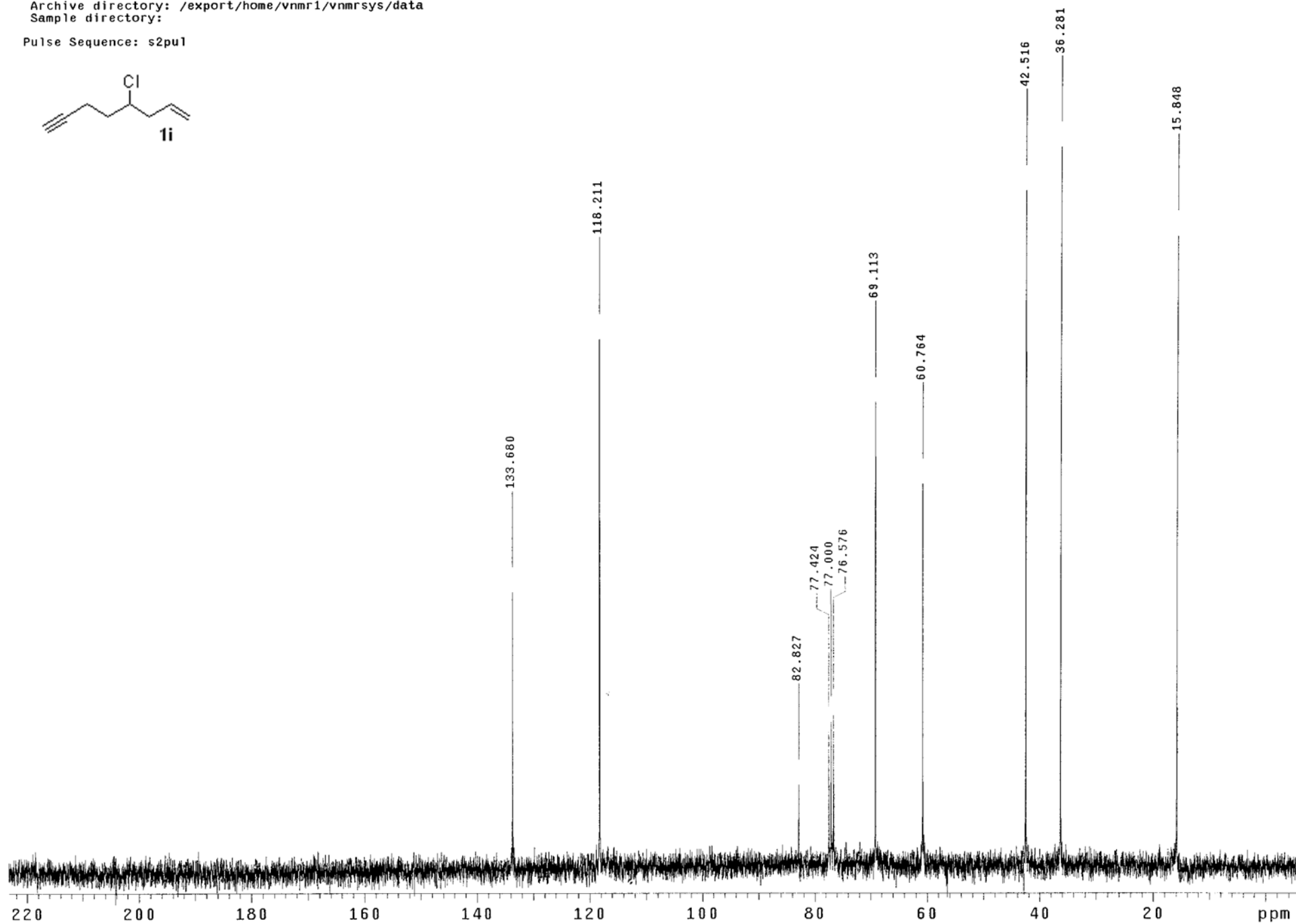
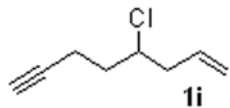
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1i-CDC13-300MHz

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Sample directory:

Pulse Sequence: s2pu1

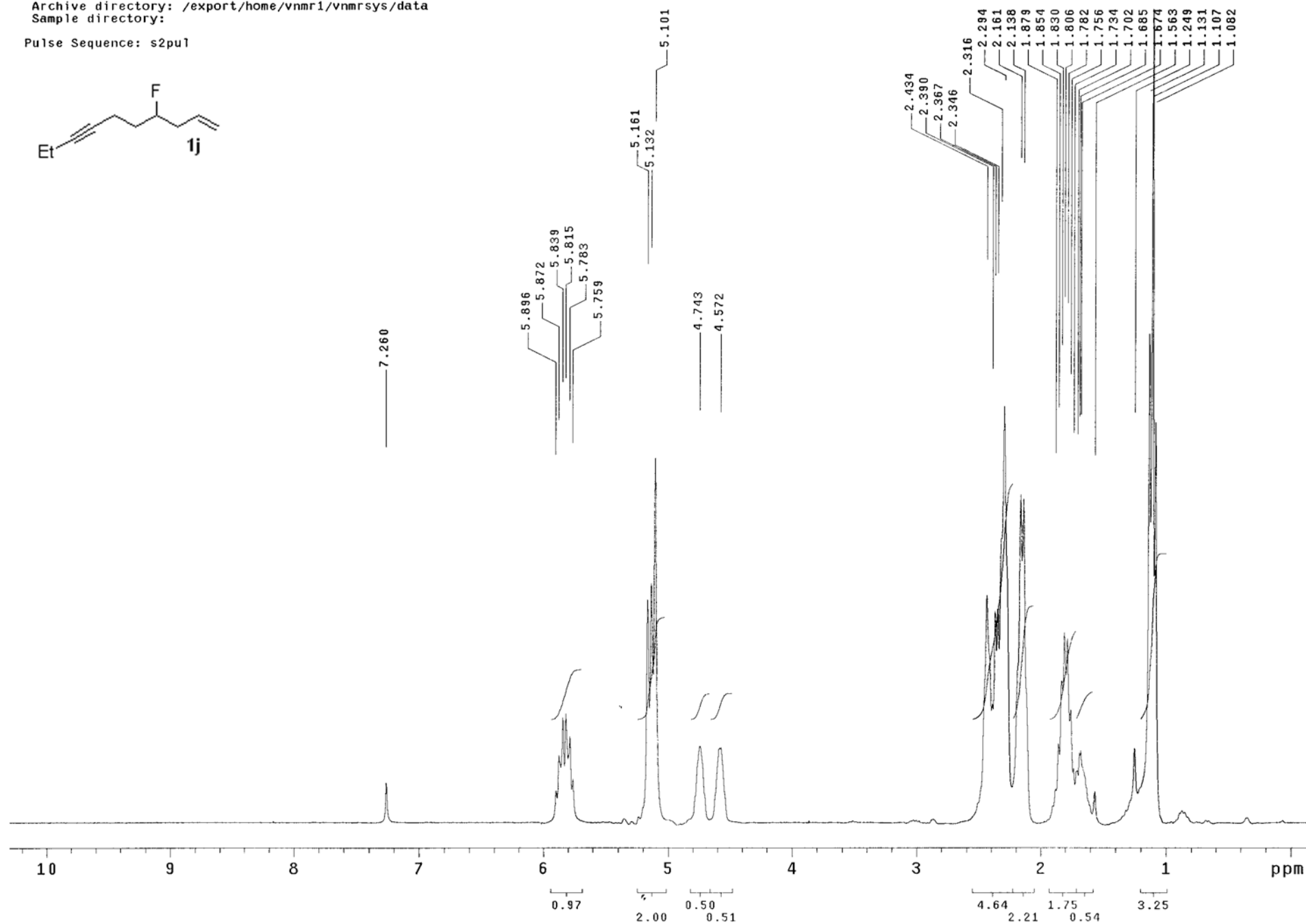
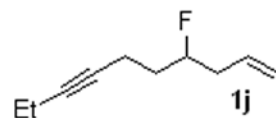


1j-CDCl3-300MHz

Archive directory: /export/home/vnmr1/vnmrsys/data

Sample directory:

Pulse Sequence: s2pu1

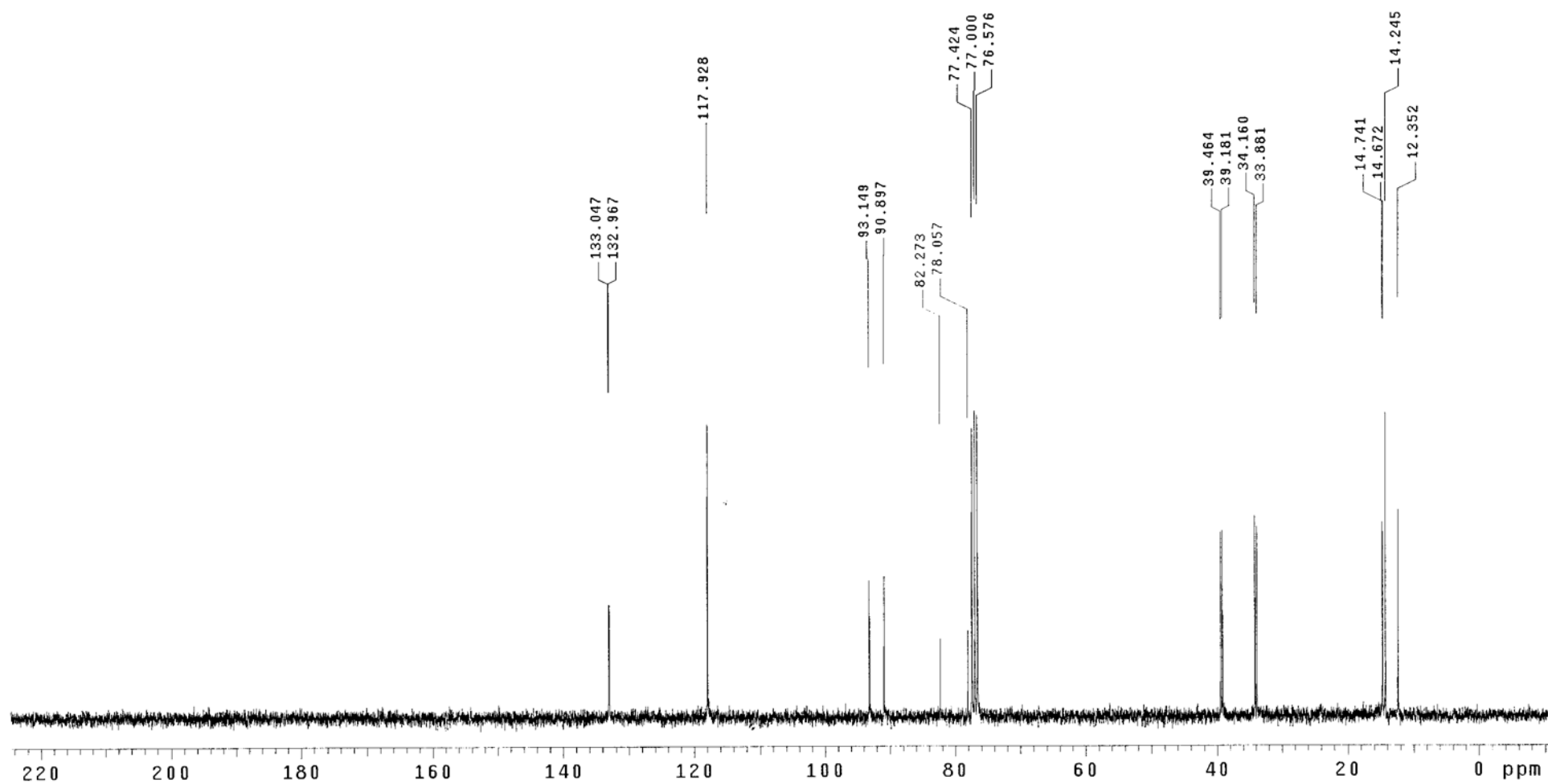
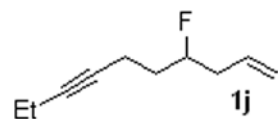


1j-CDC13-300MHz

Archive directory: /export/home/vnmr1/vnmrsys/data

Sample directory:

Pulse Sequence: s2pu1



4. HPLC chart of 1a

Shimadzu CLASS-VP V6.14 SP1

Area % Report

Page 1 of 1

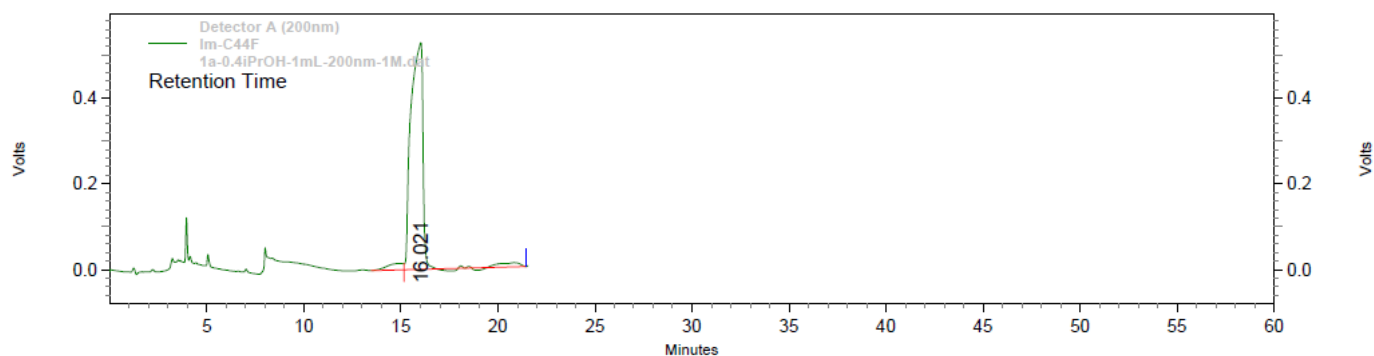
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User: System

Acquired: 2017-1-16 20:57:59

Printed: 2017-1-16 21:24:38

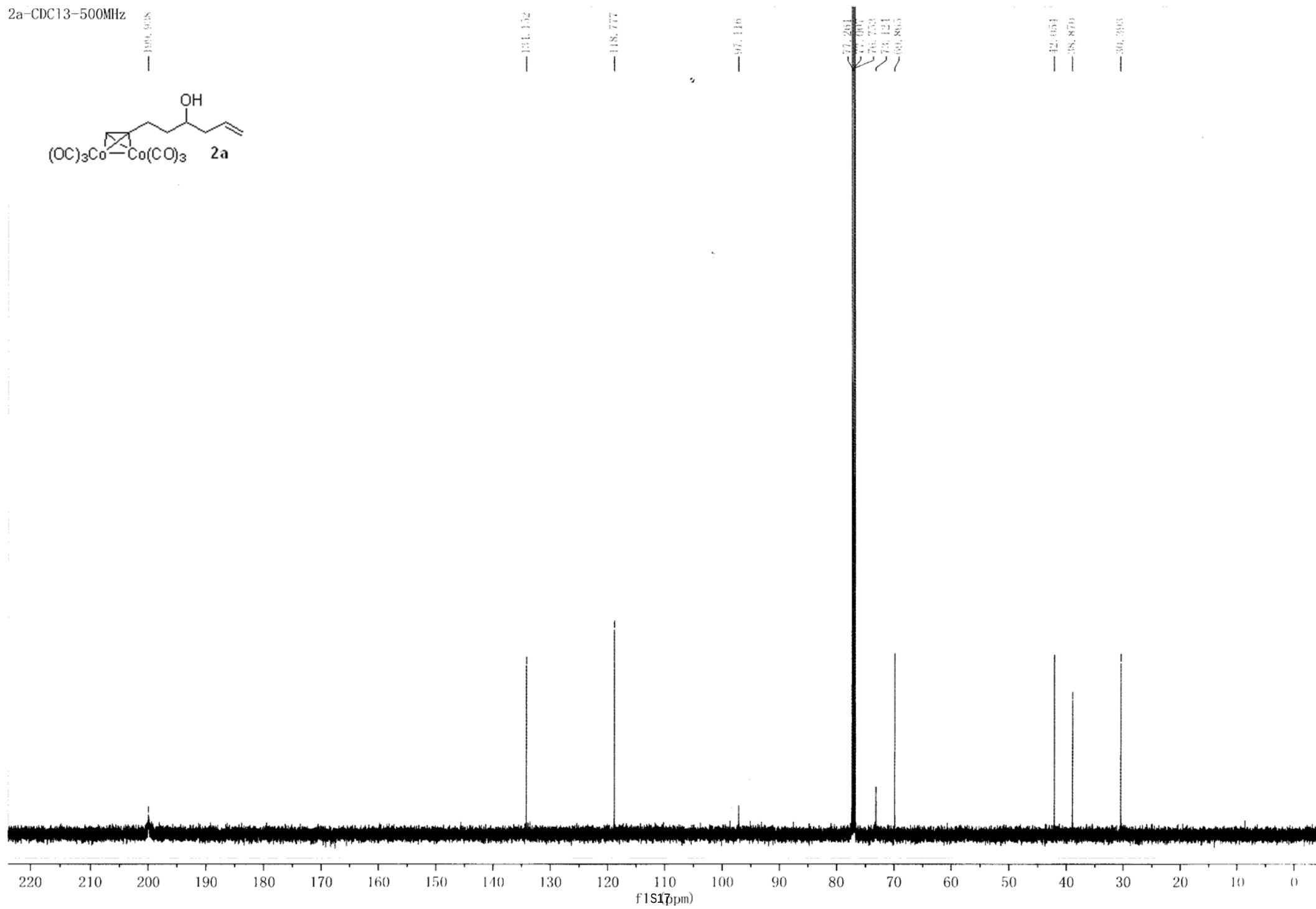
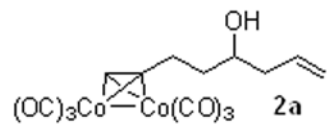


Detector A (200nm)

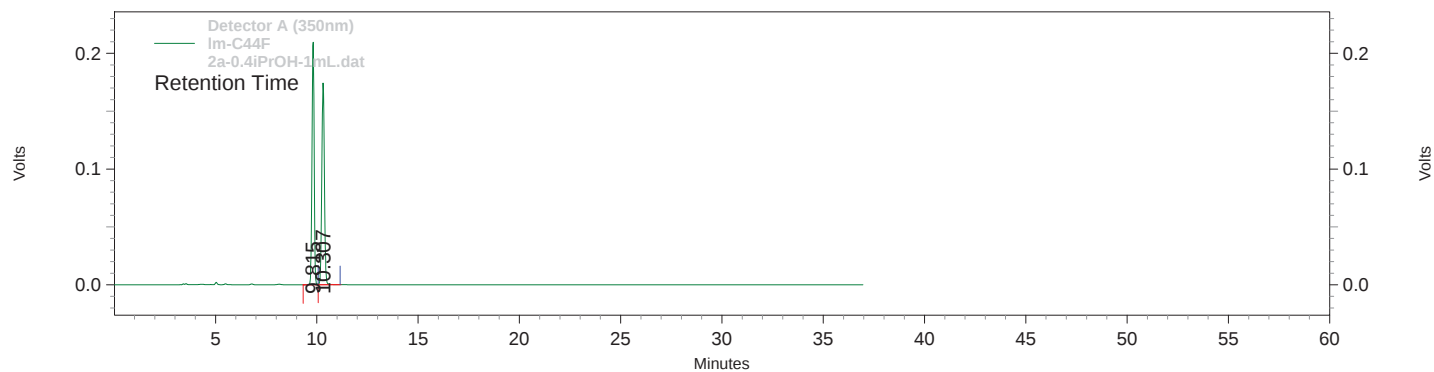
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[illegible]

2a-CDC13-500MHz



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 User: System
 Acquired: 2017-1-13 17:26:37
 Printed: 2017-1-13 18:19:03

**Detector A (350nm)**

Pk #	Retention Time	Area	Area %	Height	Height %
1	9.815	1552716	49.874	209589	54.604
2	10.307	1560583	50.126	174244	45.396

Totals		3113299	100.000	383833	100.000
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HPLC analysis of racemic 2a

.

Chiralpak-IB column

eluting solvent: 2-PrOH/n-hexane = 0.4:99.6

flow rate: 1 mL/min

column temperature: 25°C

detection wavelength: 350 nm

.

retention factors: 2.067, 2.221

selective factor: 1.075

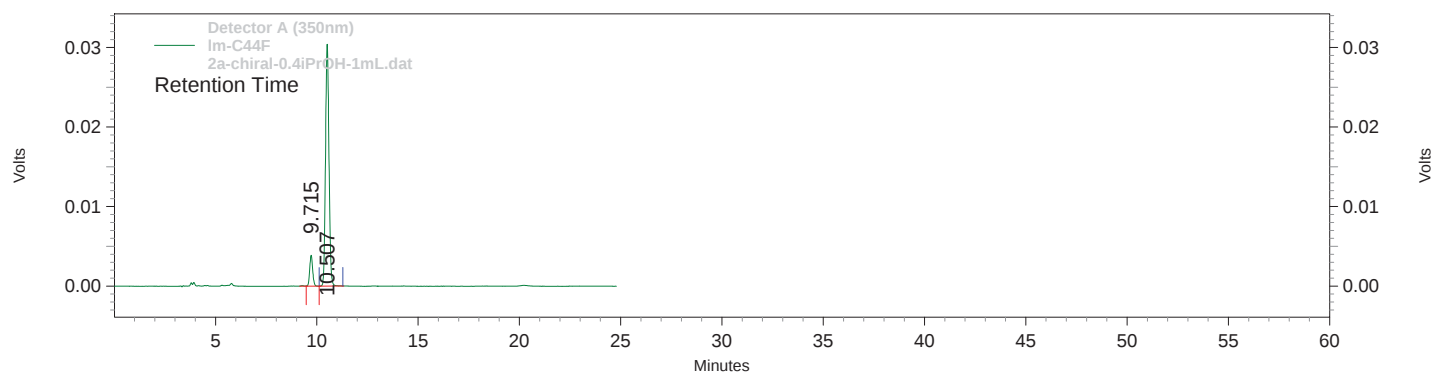
Method Name: {Method Name}

Data Name: D:\CLASS-VP6.14\Data\Xu\2a-chiral-0.4iPrOH-1mL.dat

User: System

Acquired: 2017-3-3 14:40:07

Printed: 2017-3-6 10:35:09

**Detector A (350nm)**

Pk #	Retention Time	Area	Area %	Height	Height %
1	9.715	39426	9.797	3882	11.318
2	10.507	363007	90.203	30420	88.682

Totals		402433	100.000	34303	100.000
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HPLC analysis of enantioenriched 2a

.

Chiralpak-IB column

eluting solvent: 2-PrOH/n-hexane = 0.4:99.6

flow rate: 1 mL/min

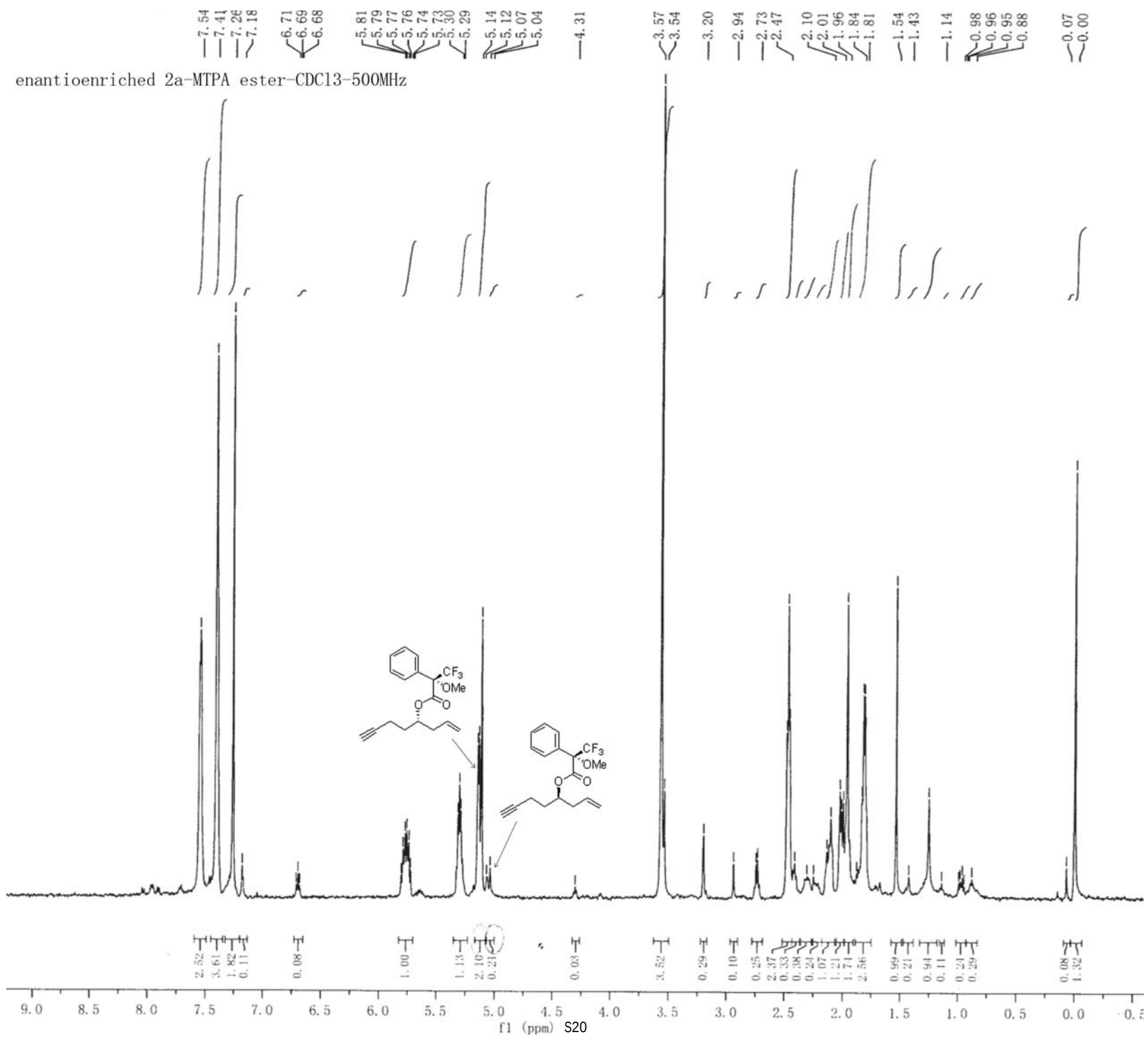
column temperature: 25°C

detection wavelength: 350 nm

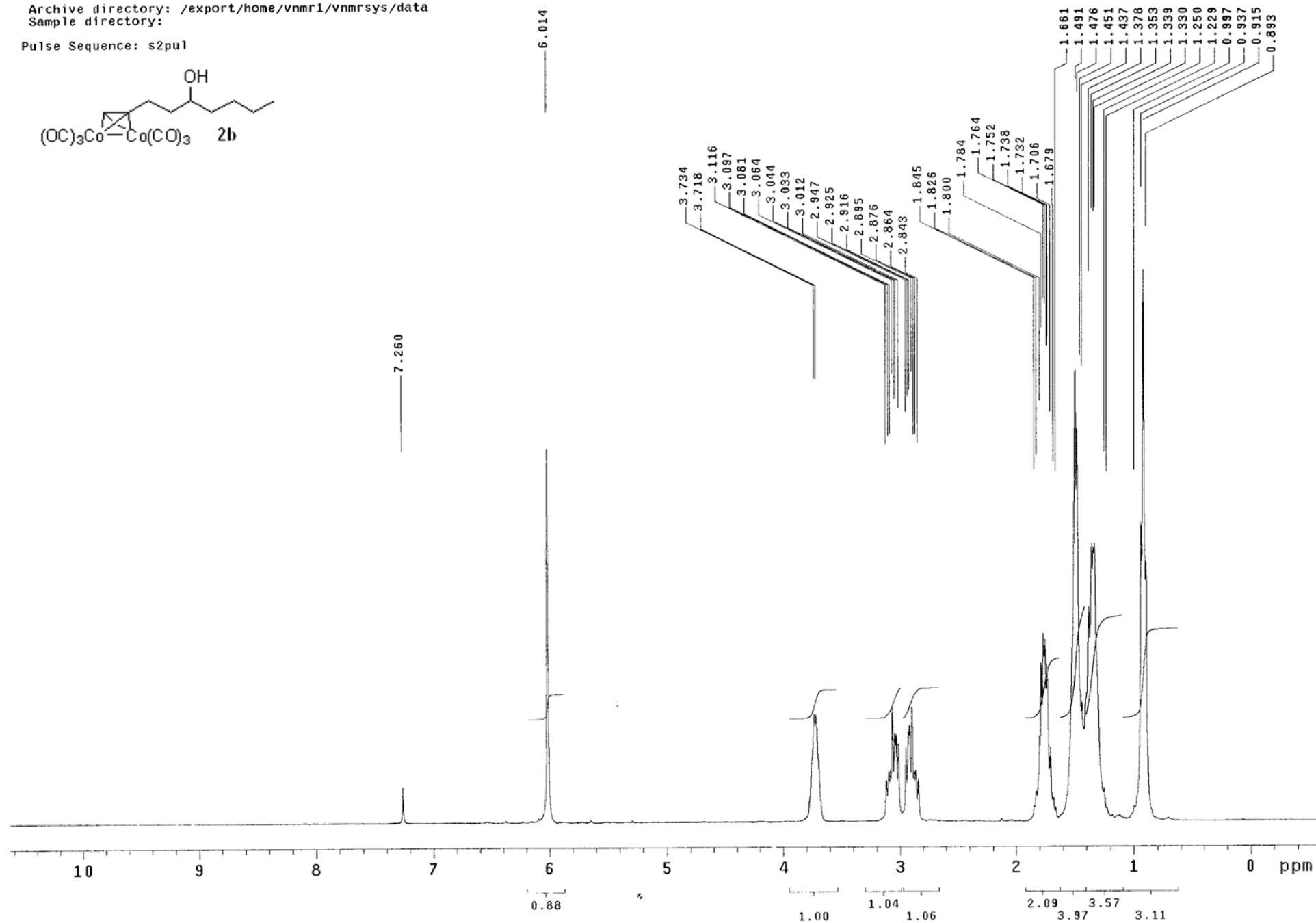
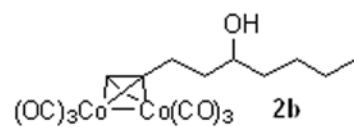
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retention factors: 2.036, 2.283

selective factor: 1.121



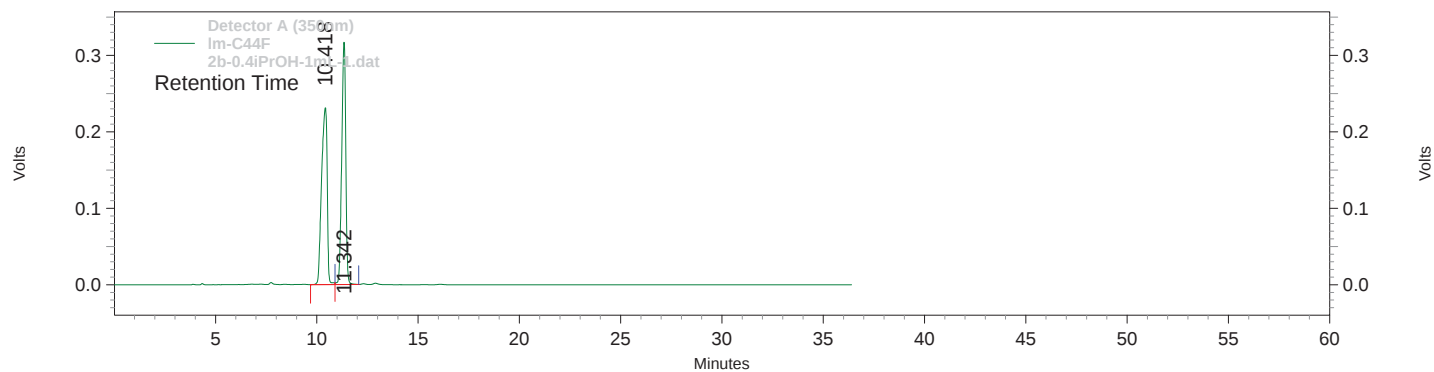
Pulse Sequence: s2pu1



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Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
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COC(=O)C1(CCCC(O)CCCC1)C(=O)OC **2b**

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 User: System
 Acquired: 2016-12-25 10:50:33
 Printed: 2017-1-6 19:54:53



Detector A (350nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	10.418	4434589	50.300	231032	42.211
2	11.342	4381753	49.700	316294	57.789

Totals		8816341	100.000	547326	100.000
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HPLC analysis of 2b

Chiralpak-IB column

eluting solvent: 2-PrOH/n-hexane = 0.4:99.6

flow rate: 1 mL/min

column temperature: 25°C

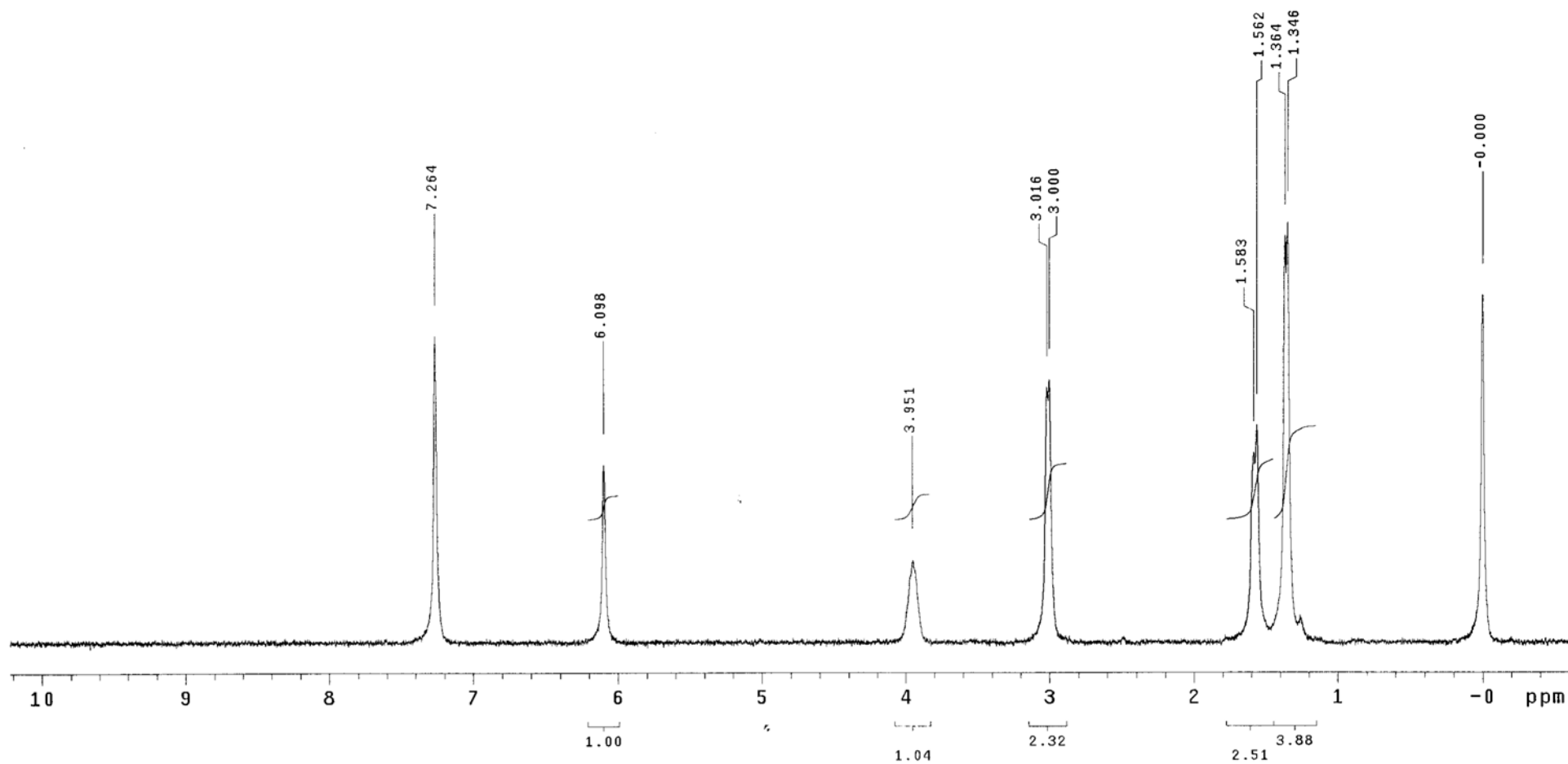
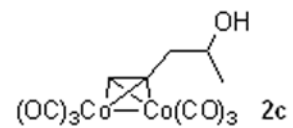
detection wavelength: 350 nm

retention factors: 2.256, 2.544

selective factor: 1.128

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Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
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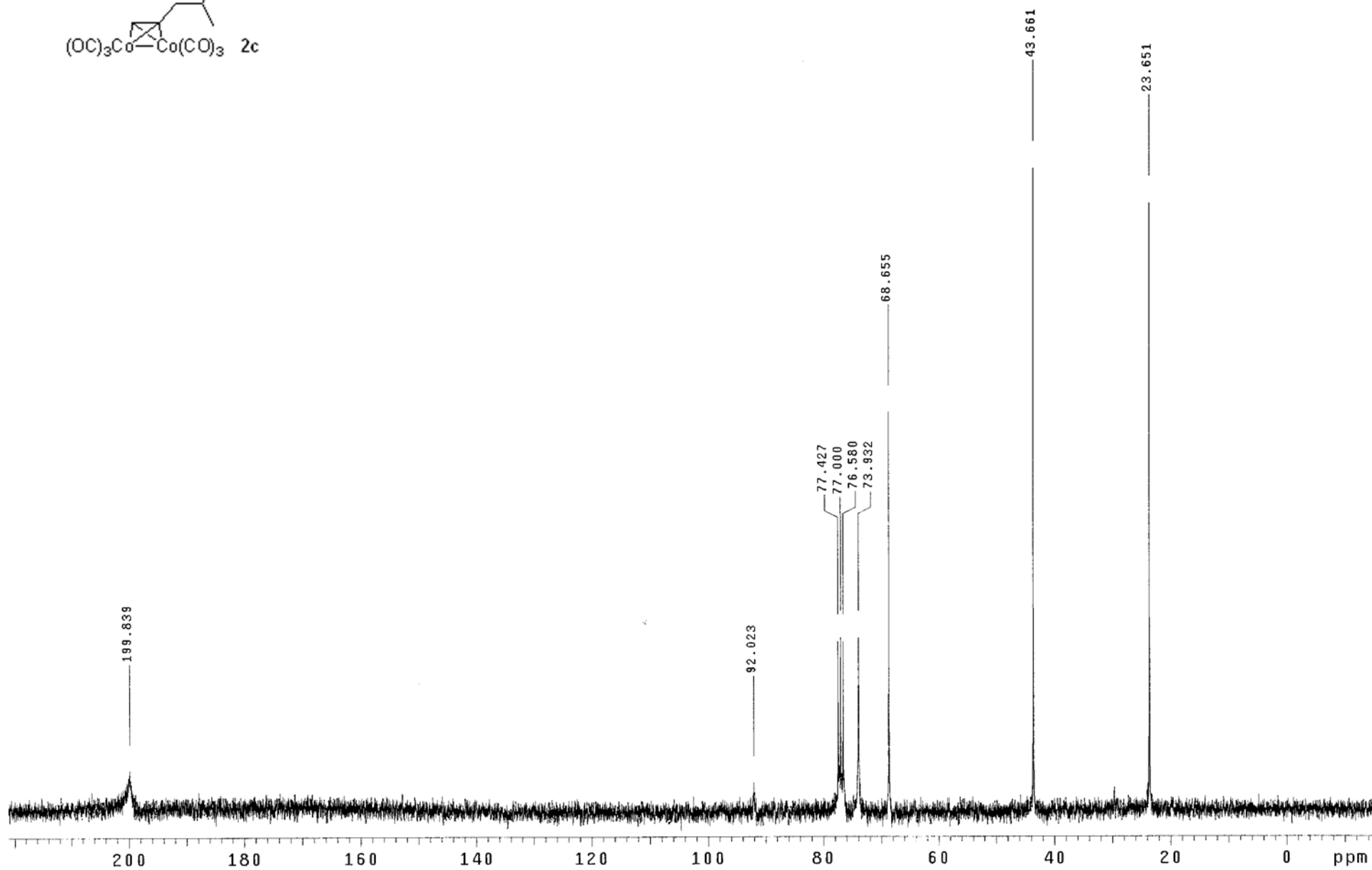
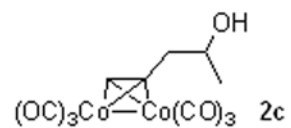
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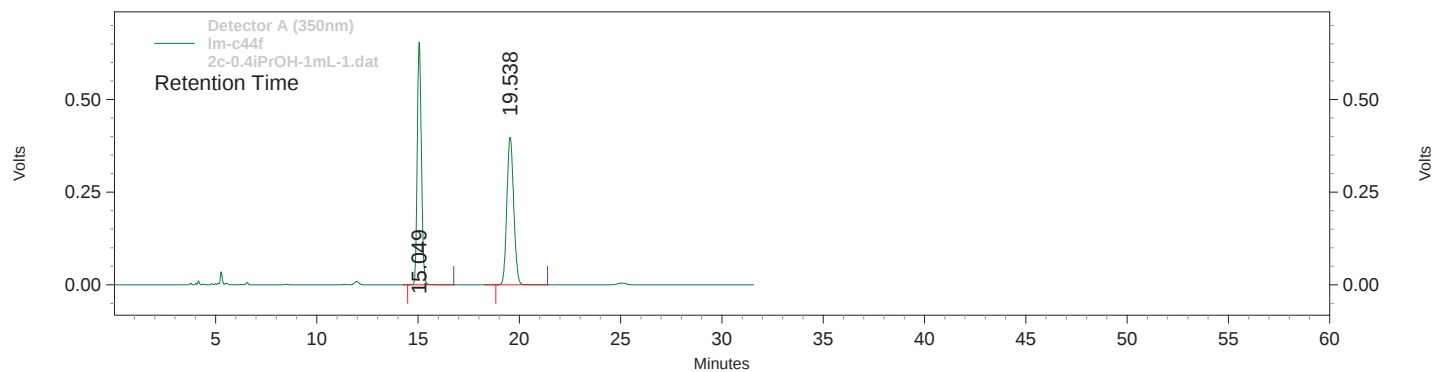
2c-CDC13-300MHz

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1



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 User: System
 Acquired: 2016-11-25 8:36:03
 Printed: 2017-1-6 14:48:08



Detector A (350nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	15.049	9328973	49.952	654684	62.179
2	19.538	9346801	50.048	398213	37.821

Totals		18675773	100.000	1052897	100.000
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HPLC analysis of 2c

Chiralpak-IB column

eluting solvent: 2-PrOH/n-hexane = 0.4:99.6

flow rate: 1 mL/min

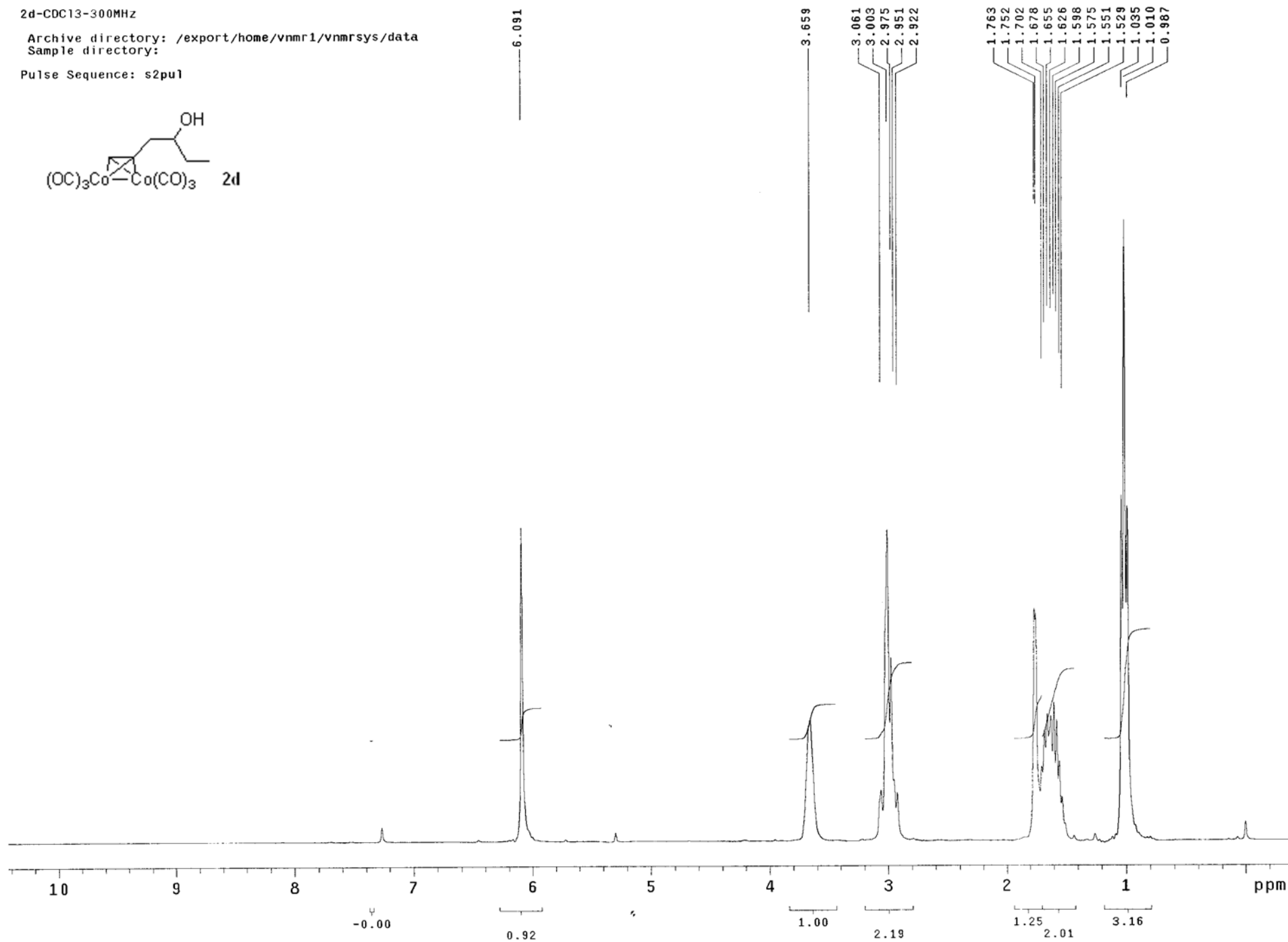
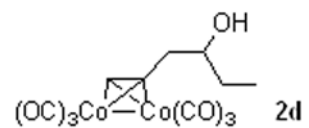
column temperature: 25°C

detection wavelength: 350 nm

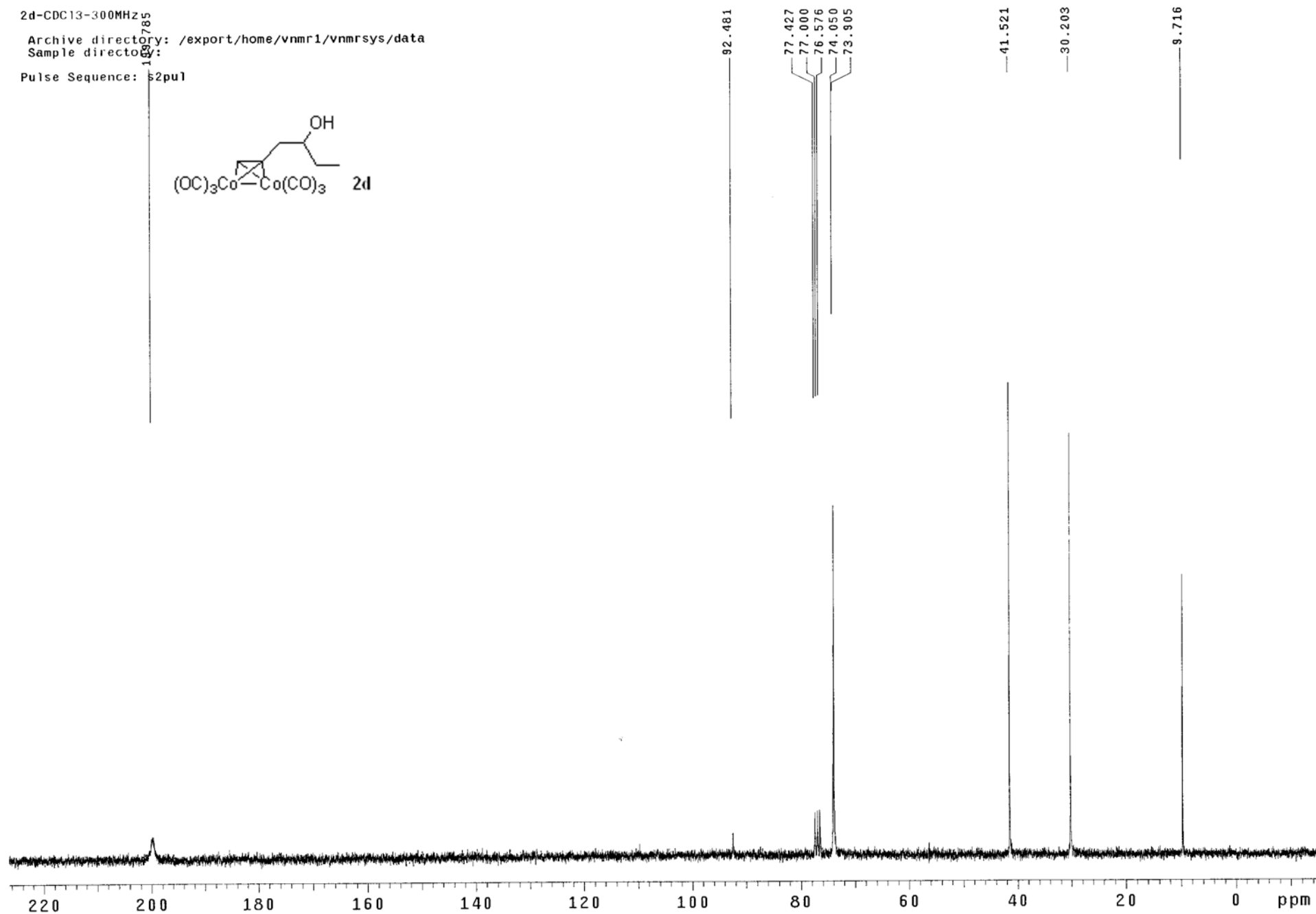
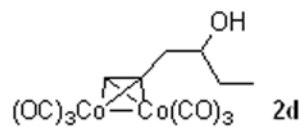
retention factors: 3.703, 5.106

selective factor: 1.379

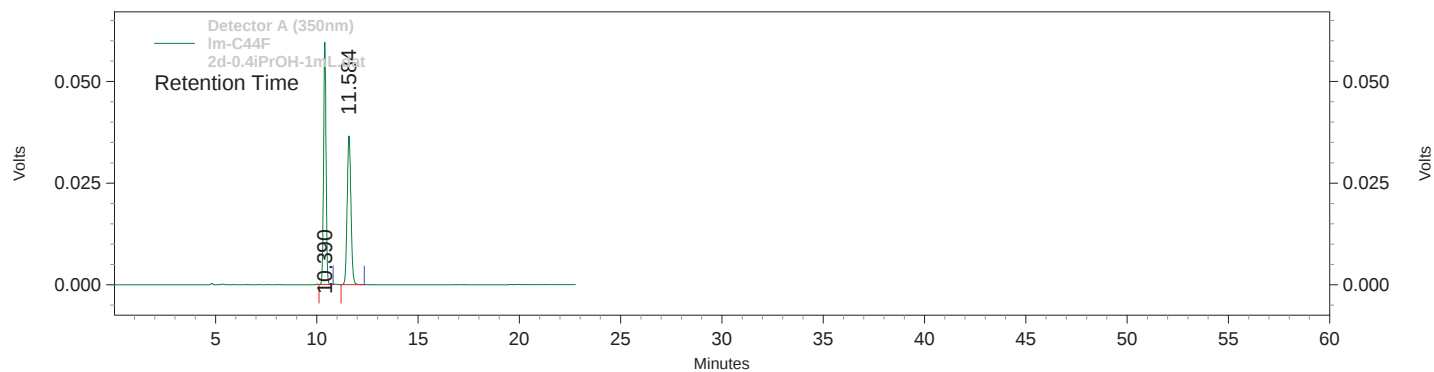
Pulse Sequence: s2pu1



Pulse Sequence: s2pul



Method Name: C:\CLASS-VP\untitled.met
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 User: System
 Acquired: 2016-12-2 18:37:20
 Printed: 2017-1-6 20:35:40



Detector A (350nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	10.390	499308	51.300	59062	61.800
2	11.584	474009	48.700	36507	38.200

Totals		973316	100.000	95569	100.000
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HPLC analysis of 2d

Chiralpak-IB column

eluting solvent: 2-PrOH/n-hexane = 0.4:99.6

flow rate: 1 mL/min

column temperature: 25°C

detection wavelength: 350 nm

retention factors: 2.247, 2.620

selective factor: 1.166

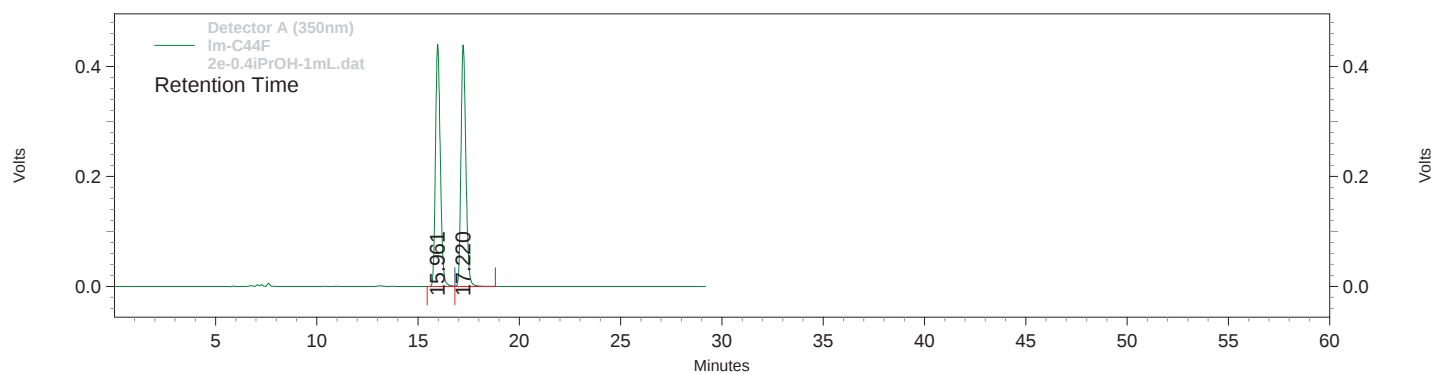
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Sample directory: gyl3-37-A
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[illegible]

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Archive directory: /home/vjwalk/vnmrsys/data/2017Jan/vjwalk
Sample directory: gyl3-37-A
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CC(C)C(O)C1C2C(C1)C(C2)C3(CO3)Co(CO)Co(CO)C3 2e

Method Name: C:\CLASS-VP\untitled.met
 Data Name: D:\CLASS-VP6.14\Data\Xu\2e-0.4iPrOH-1mL.dat
 User: System
 Acquired: 2016-12-5 15:15:43
 Printed: 2017-1-6 20:01:55

**Detector A (350nm)**

Pk #	Retention Time	Area	Area %	Height	Height %
1	15.961	7354877	50.005	440714	50.091
2	17.220	7353289	49.995	439117	49.909

Totals		14708166	100.000	879831	100.000
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HPLC analysis of 2e

.

Chiralpak-IB column

eluting solvent: 2-PrOH/n-hexane = 0.4:99.6

flow rate: 1 mL/min

column temperature: 25°C

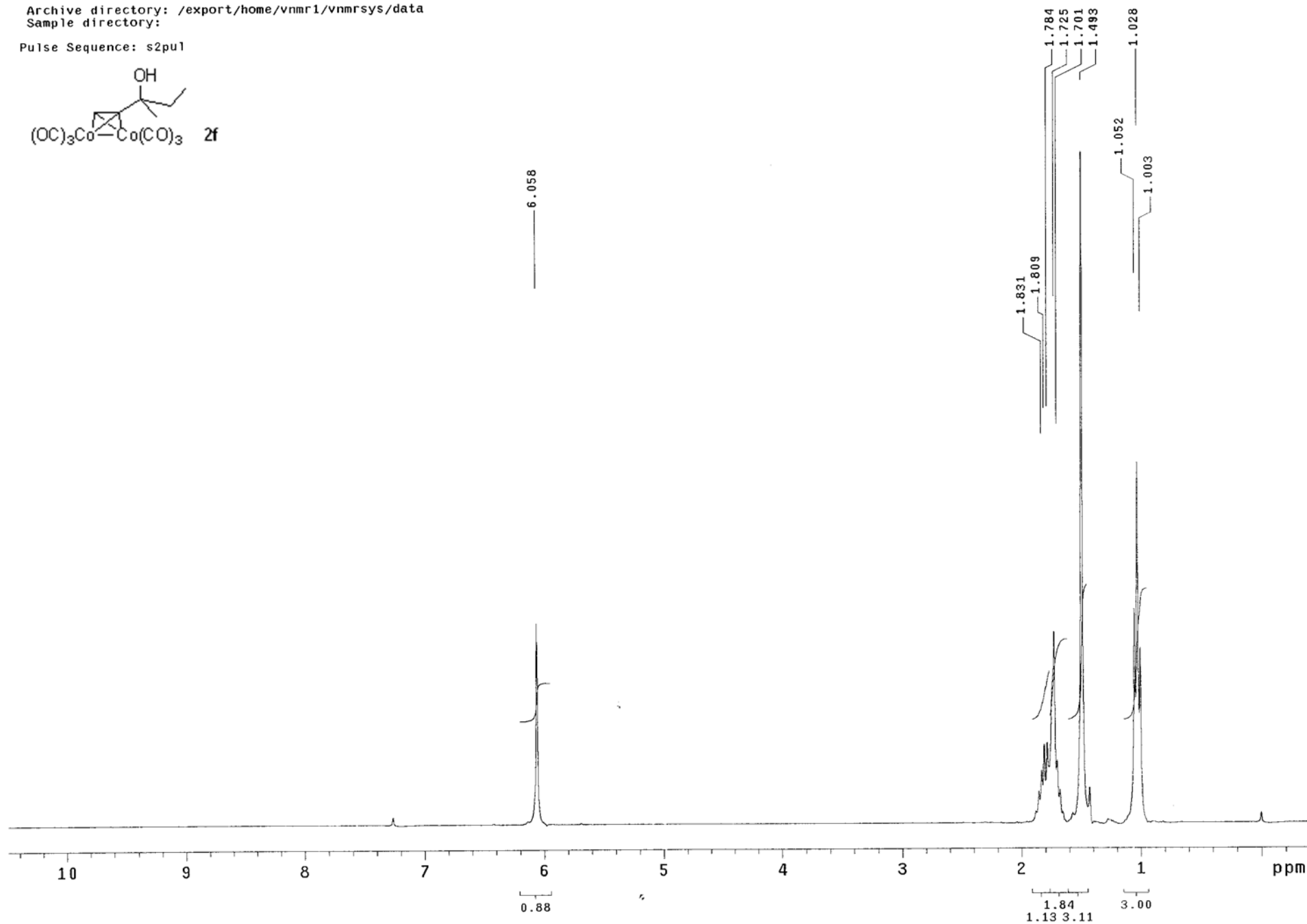
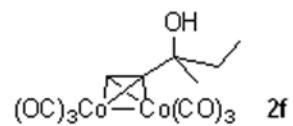
detection wavelength: 350 nm

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retention factors: 3.988, 4.381

selective factor: 1.099

Pulse Sequence: s2pu1

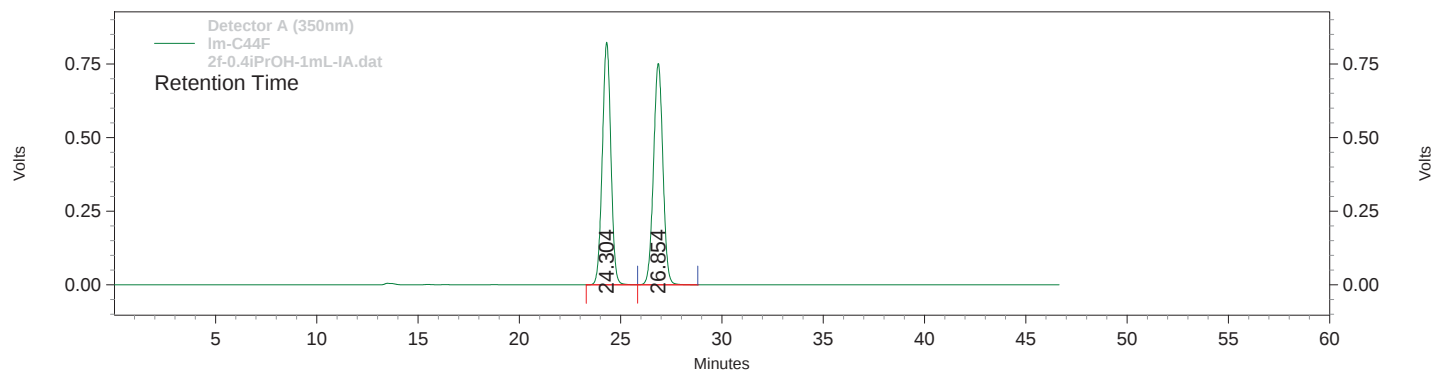


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Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
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(OC)₃Co—Co(CO)₃ 2f



Method Name: C:\CLASS-VP\untitled.met
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 User: System
 Acquired: 2016-12-9 10:28:18
 Printed: 2017-1-6 20:07:03



Detector A (350nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	24.304	24231407	49.944	823853	52.303
2	26.854	24285445	50.056	751314	47.697

Totals		48516852	100.000	1575168	100.000
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Chiralpak-IA column

eluting solvent: 2-PrOH/n-hexane = 0.4:99.6

flow rate: 1 mL/min

column temperature: 25°C

detection wavelength: 350 nm

.

retention factors: 6.815, 7.635

selective factor: 1.120

```
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
```

2g

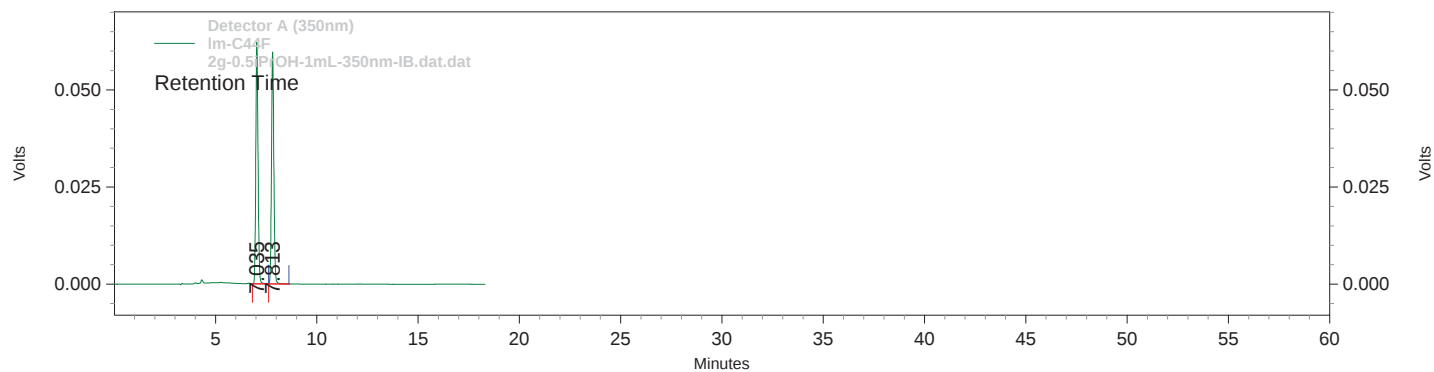


```
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
```

2g



Method Name: C:\CLASS-VP\untitled.met
 Data Name: D:\CLASS-VP6.14\Data\Xu\2g-0.5iPrOH-1mL-350nm-IB.dat.dat
 User: System
 Acquired: 2017-1-10 9:58:57
 Printed: 2017-1-18 15:31:30

**Detector A (350nm)**

Pk #	Retention Time	Area	Area %	Height	Height %
1	7.035	479562	50.013	62149	50.992
2	7.813	479316	49.987	59729	49.008

Totals		958878	100.000	121878	100.000
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HPLC analysis of 2g

Chiralpak-IB column

eluting solvent: 2-PrOH/n-hexane = 0.5:99.5

flow rate: 1 mL/min

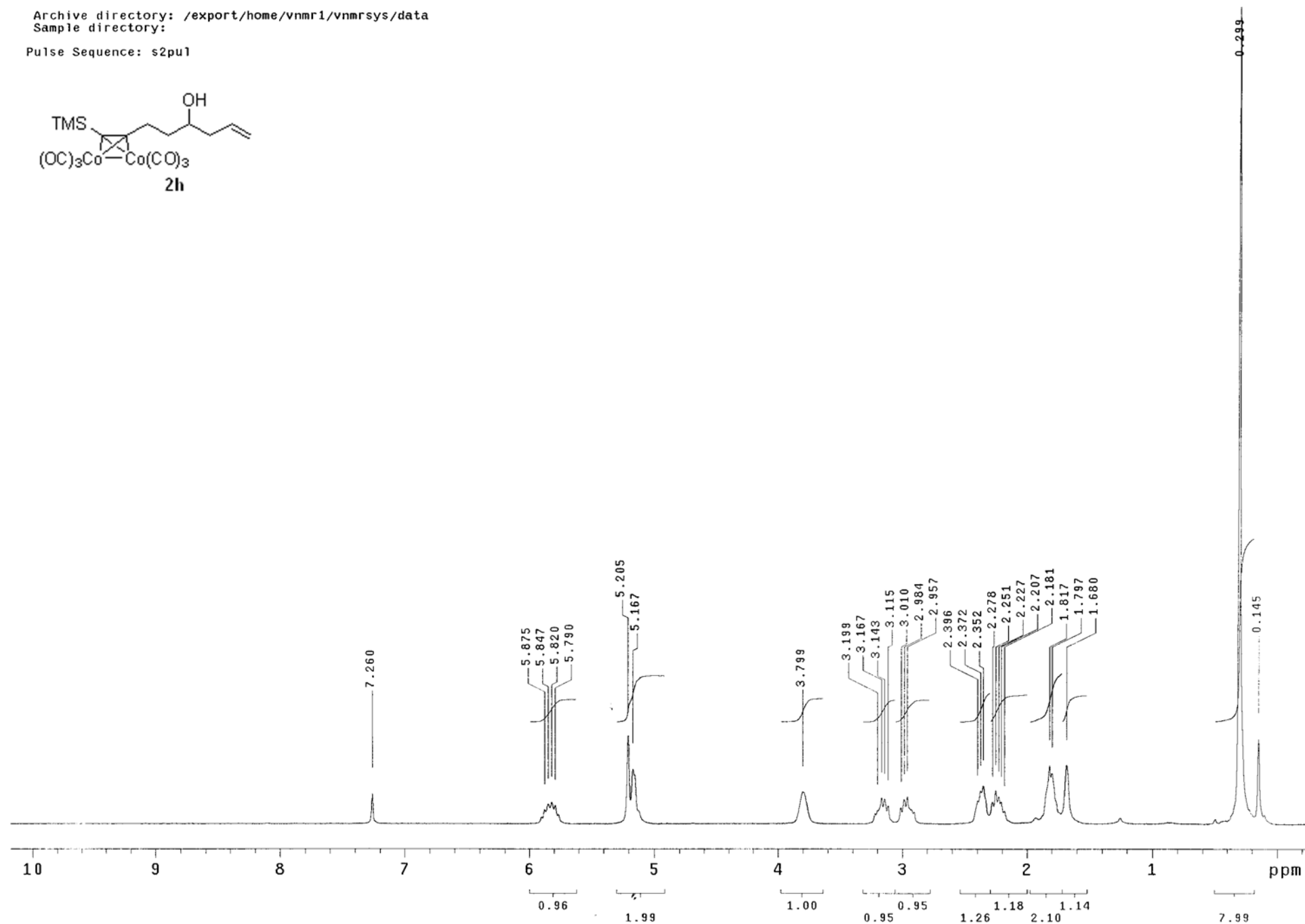
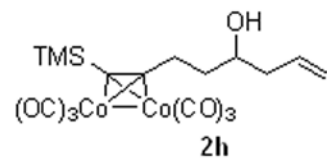
column temperature: 25°C

detection wavelength: 350 nm

retention factors: 1.198, 1.441

selective factor: 1.203

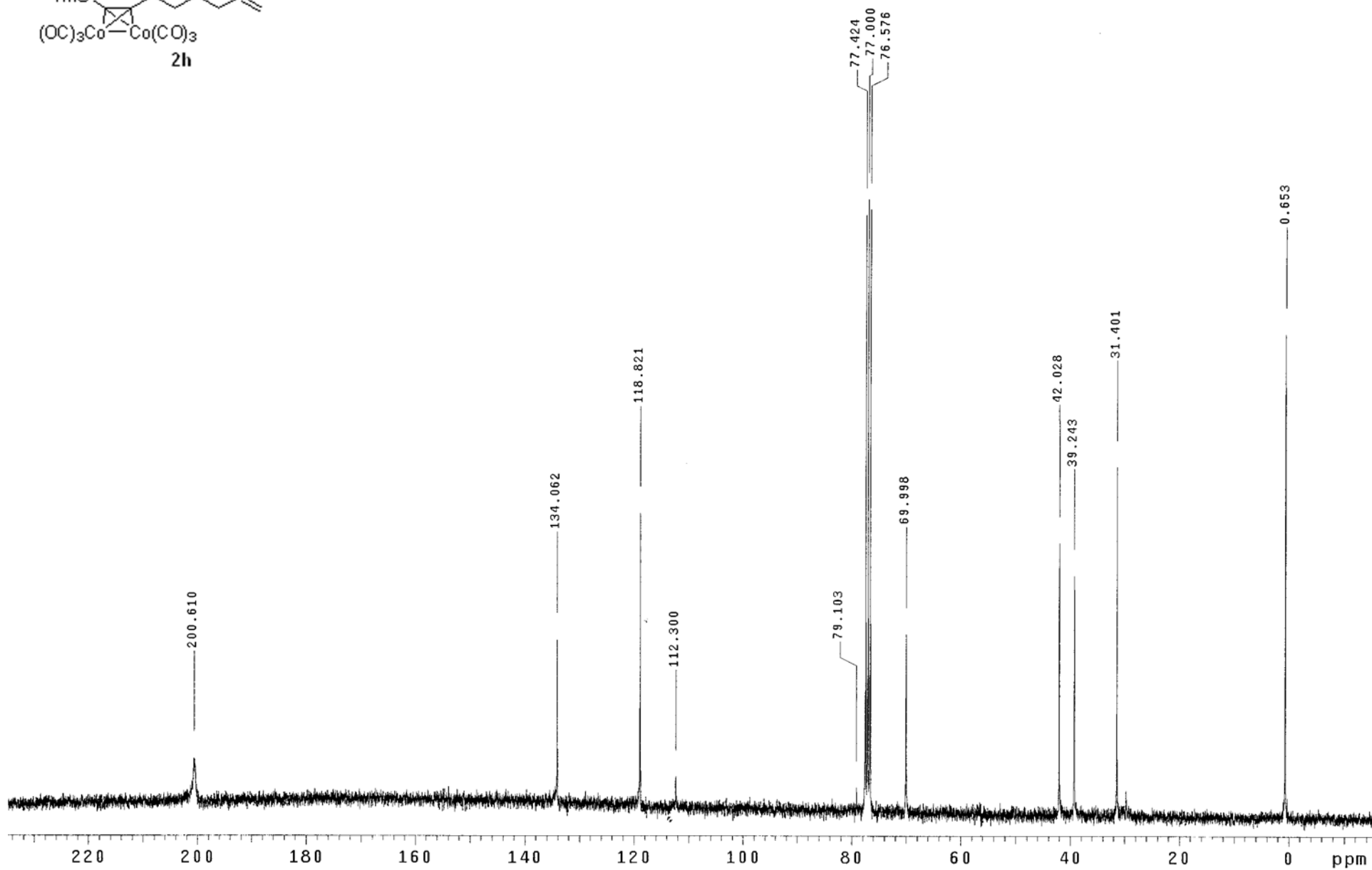
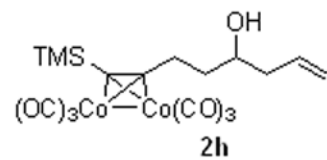
Pulse Sequence: s2pu1



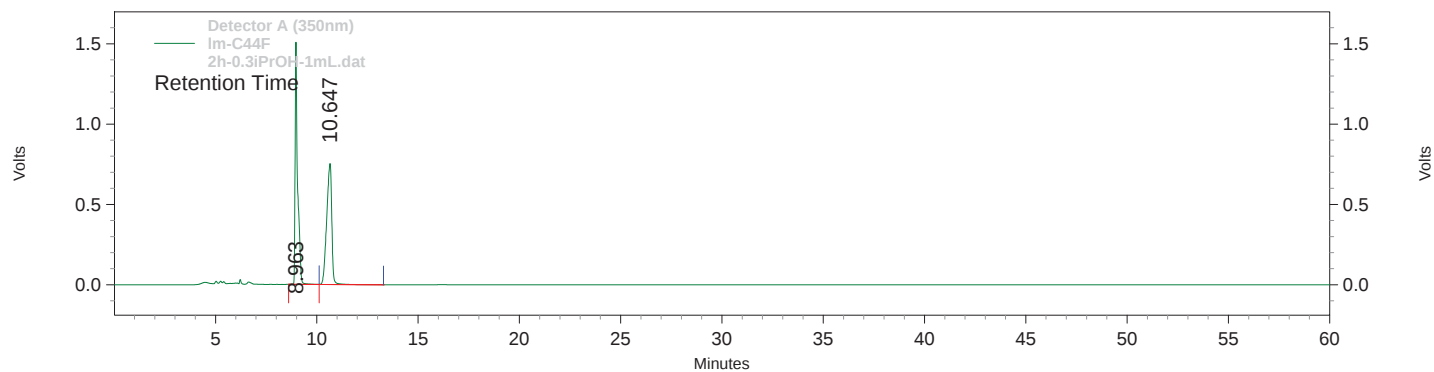
2h-CDC13-300MHz

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1



Method Name: C:\CLASS-VP\untitled.met
 Data Name: D:\CLASS-VP6.14\Data\Xu\2h-0.3iPrOH-1mL.dat
 User: System
 Acquired: 2016-12-20 8:18:50
 Printed: 2017-1-18 15:33:21

**Detector A (350nm)**

Pk #	Retention Time	Area	Area %	Height	Height %
1	8.963	12932161	49.699	1507716	66.686
2	10.647	13088602	50.301	753217	33.314

Totals		26020763	100.000	2260934	100.000
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HPLC analysis of 2h

Chiralpak-IB column

eluting solvent: 2-PrOH/n-hexane = 0.3:99.7

flow rate: 1 mL/min

column temperature: 25°C

detection wavelength: 350 nm

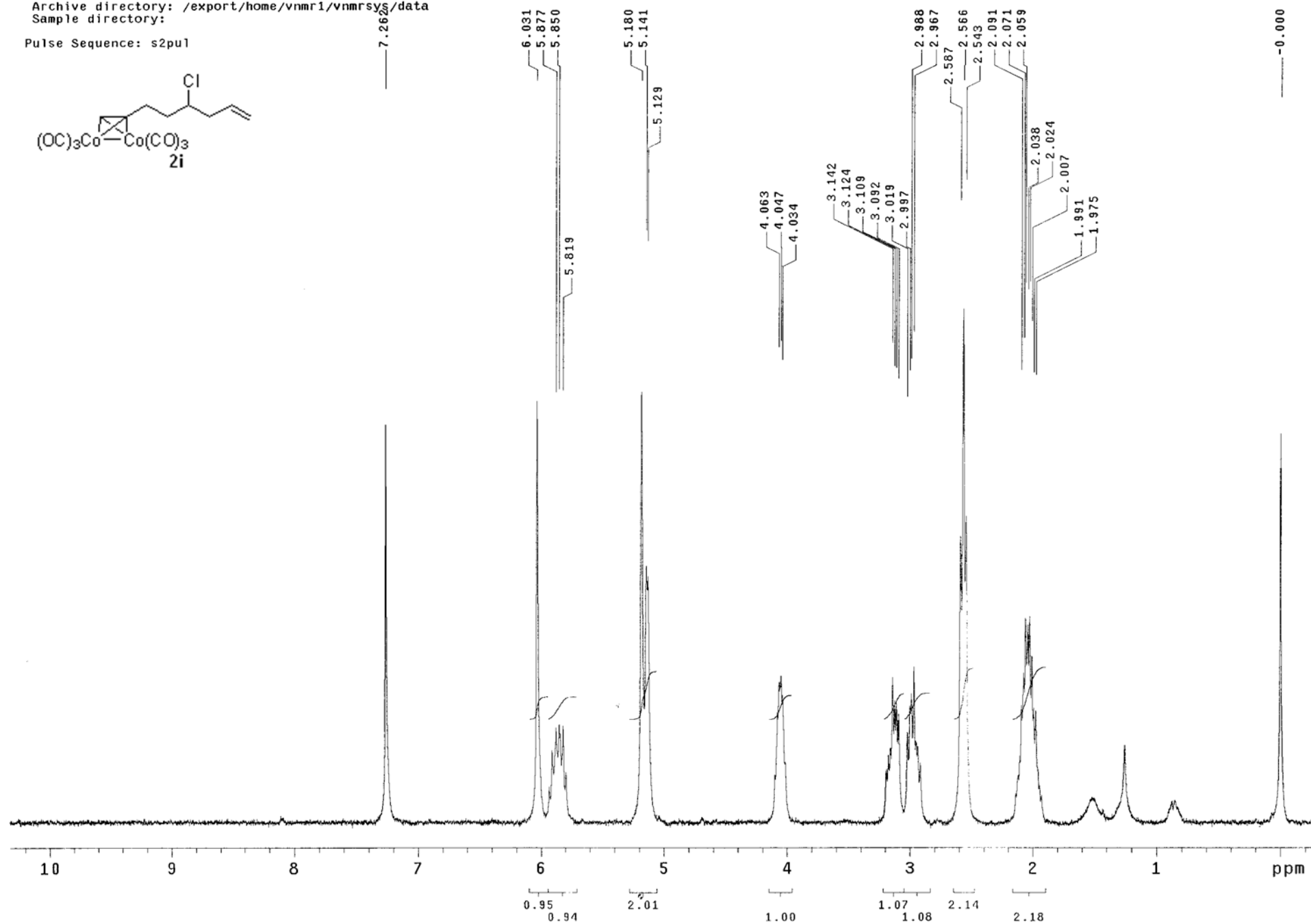
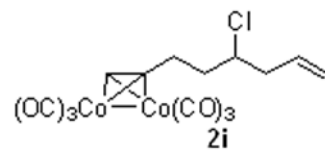
retention factors: 1.801, 2.327

selective factor: 1.292

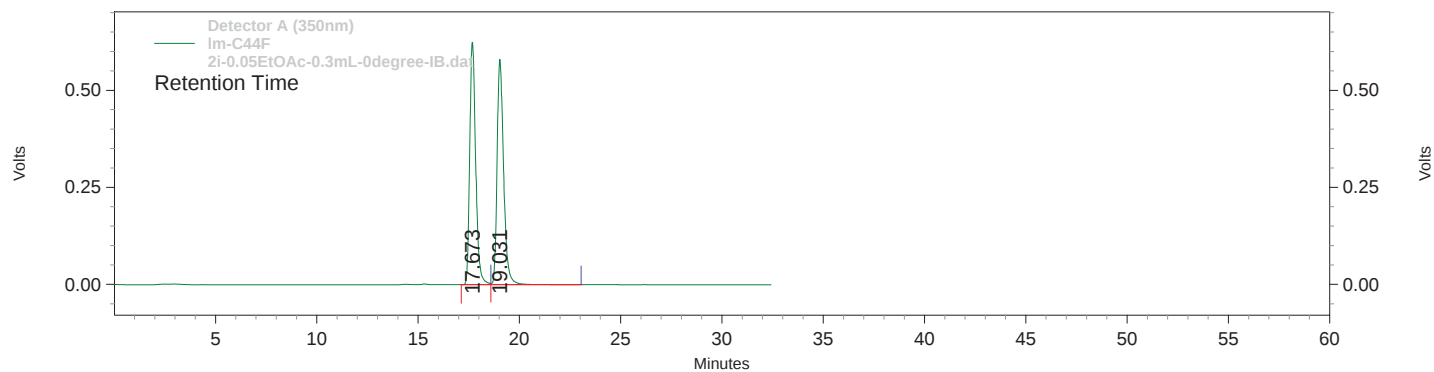
2i-CDC13-300MHz

Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:

Pulse Sequence: s2pu1



Method Name: C:\CLASS-VP\untitled.met
 Data Name: D:\CLASS-VP6.14\Data\Xu\2i-0.05EtOAc-0.3mL-0degree-IB.dat
 User: System
 Acquired: 2017-1-5 12:35:45
 Printed: 2017-1-18 15:34:27



Detector A (350nm)

Pk #	Retention Time	Area	Area %	Height	Height %
1	17.673	12770343	49.463	624814	51.834
2	19.031	13047813	50.537	580604	48.166

Totals		25818156	100.000	1205419	100.000
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HPLC analysis of 2i

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Chiralpak-IB column

eluting solvent: EtOAc/n-hexane = 0.05:99.95

flow rate: 0.3 mL/min

column temperature: 0°C

detection wavelength: 350 nm

.

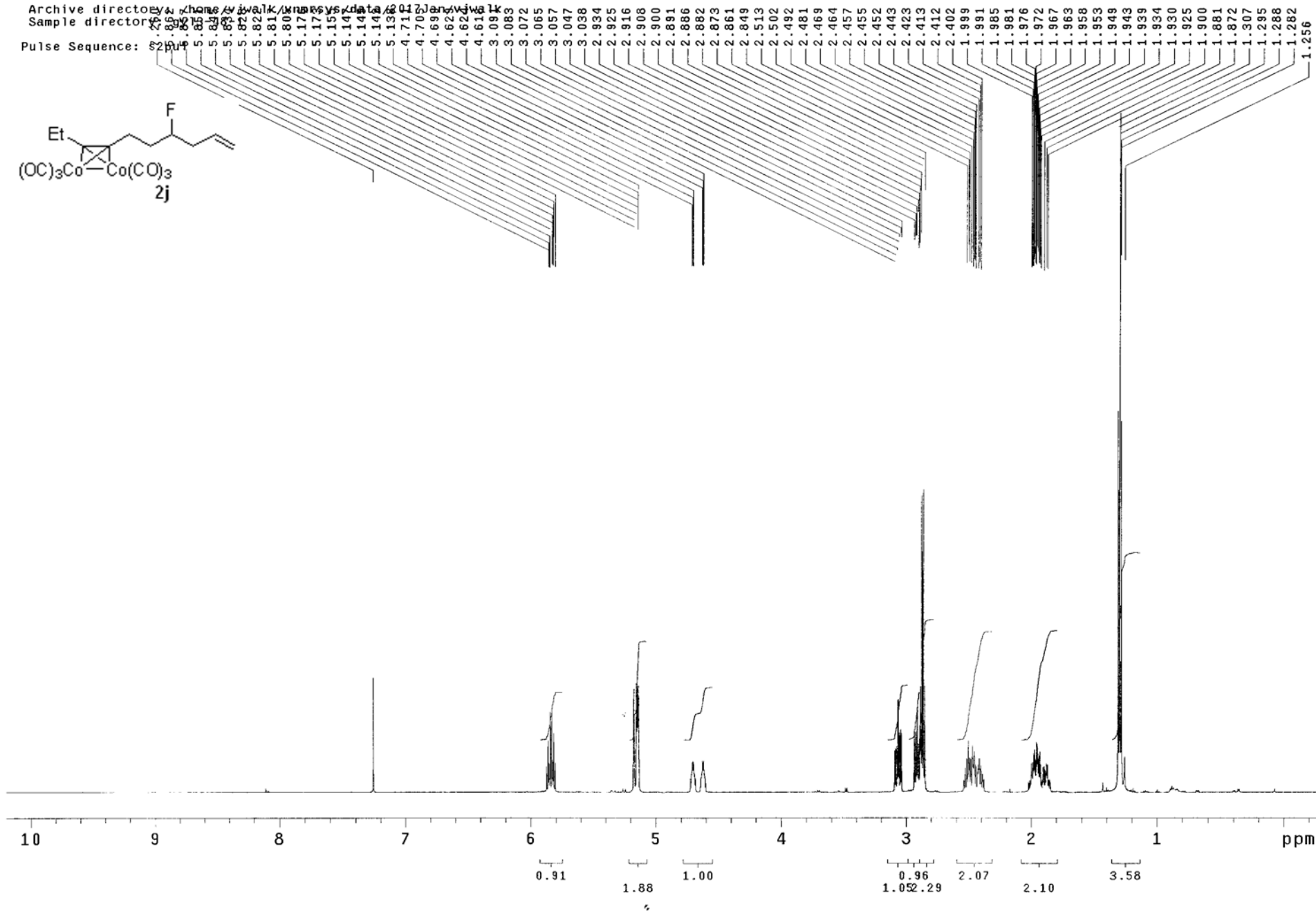
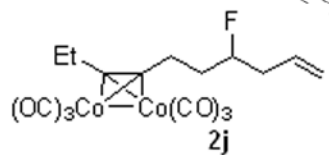
retention factors: 0.592, 0.715

selective factor: 1.208

Archive directory: home\jwalk\analysis\data\2017Jan\2jwalk

Sample directory: 2jwalk

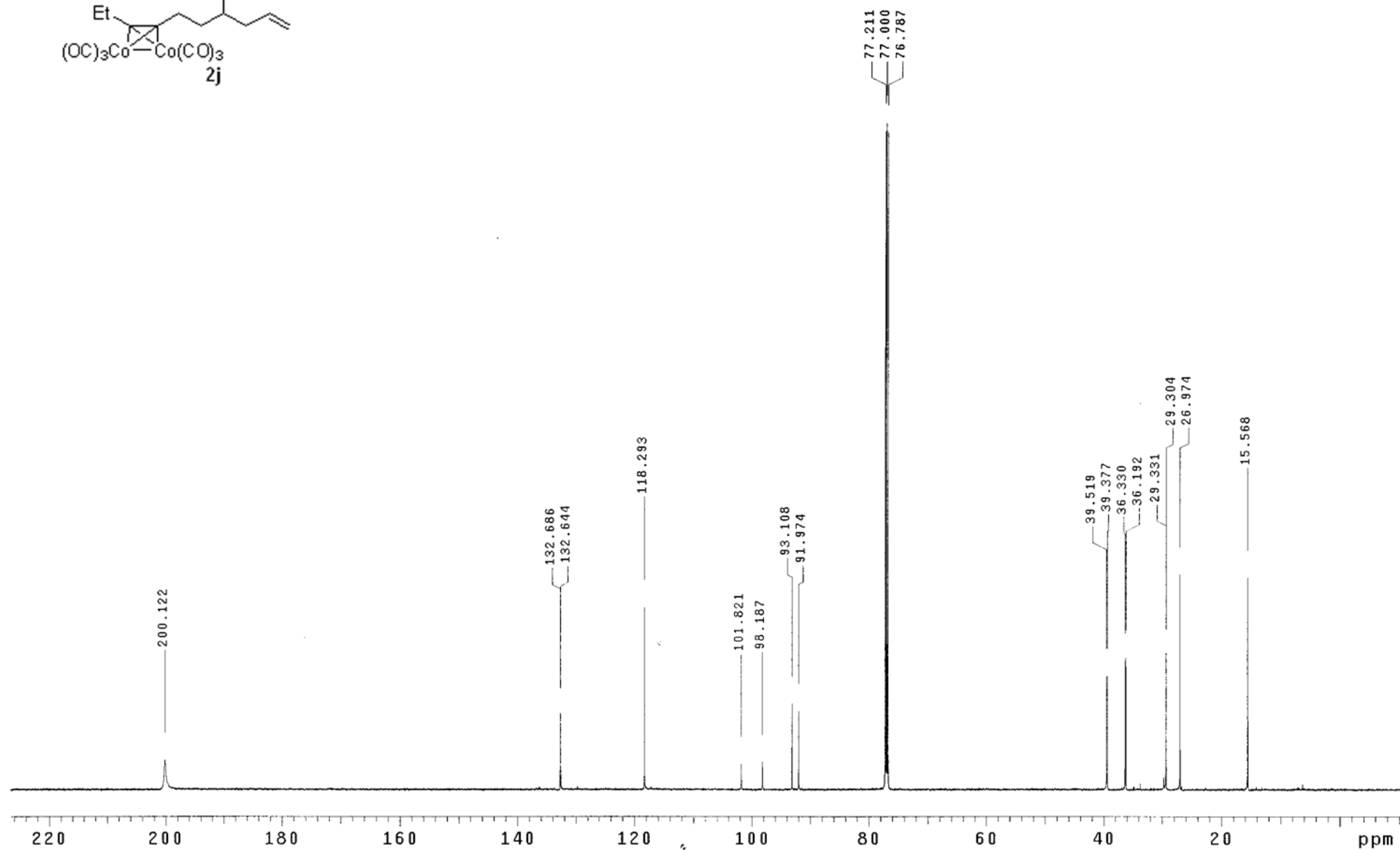
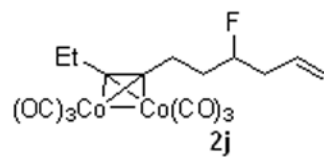
Pulse Sequence: zgpg30



2j-CDC13-600MHz

Archive directory: /home/vjwalk/vnmrsys/data/2017Jan/vjwalk
Sample directory: gy13-48-1

Pulse Sequence: s2pul1



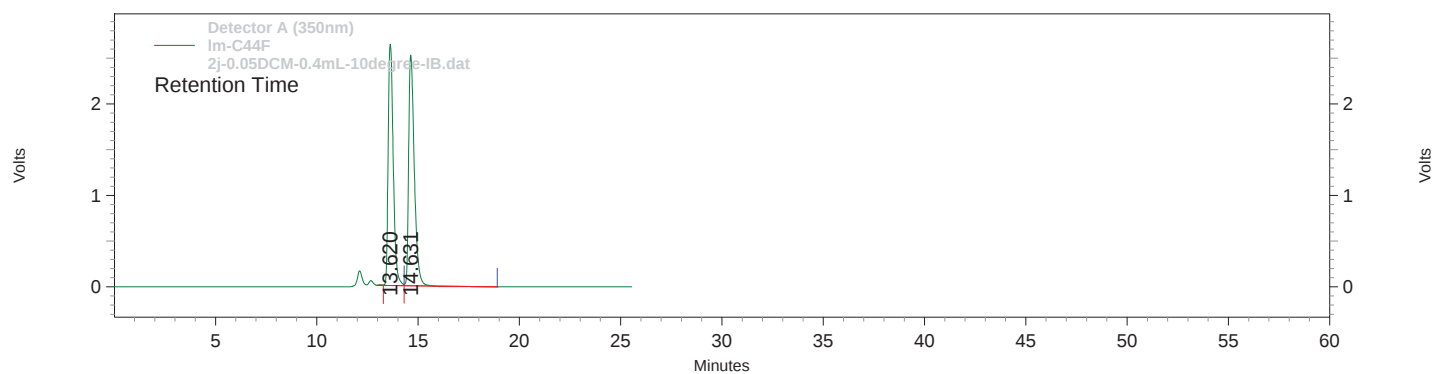
Method Name: {Method Name}

Data Name: D:\CLASS-VP6.14\Data\Xu\2j-0.05DCM-0.4mL-10degree-IB.dat

User: System

Acquired: 2017-1-9 11:45:14

Printed: 2017-3-6 14:40:08

**Detector A (350nm)**

Pk #	Retention Time	Area	Area %	Height	Height %
1	13.620	45829535	48.746	2639148	51.178
2	14.631	48186864	51.254	2517634	48.822

Totals		94016399	100.000	5156782	100.000
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HPLC analysis of 2j

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Chiralpak-IB column

eluting solvent: CH₂Cl₂/n-hexane = 0.05:99.95

flow rate: 0.4 mL/min

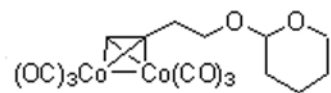
column temperature: 10°C

detection wavelength: 350 nm

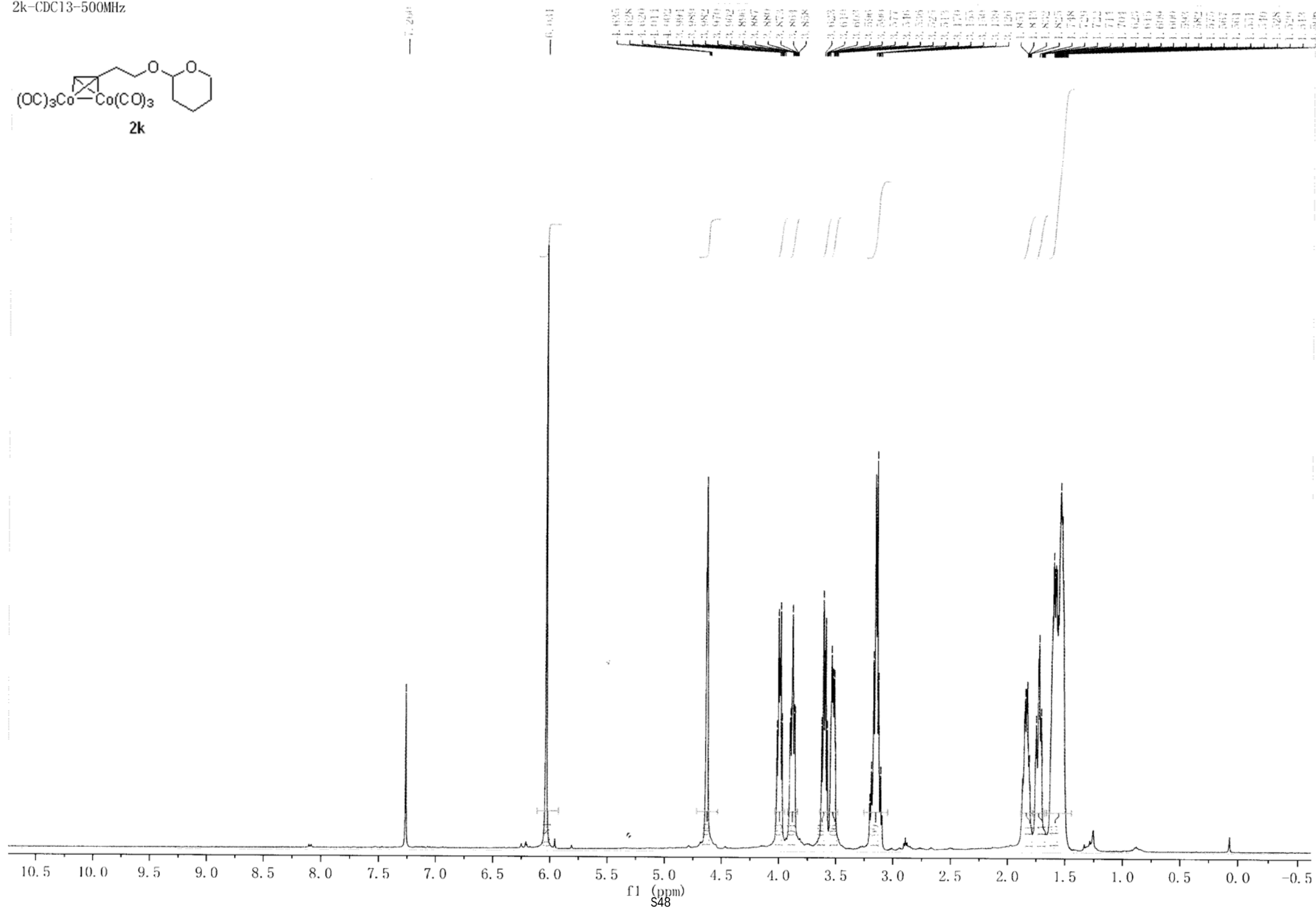
.

retention factors: 0.584, 0.701

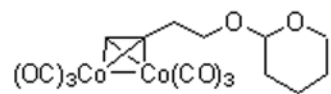
selective factor: 1.200



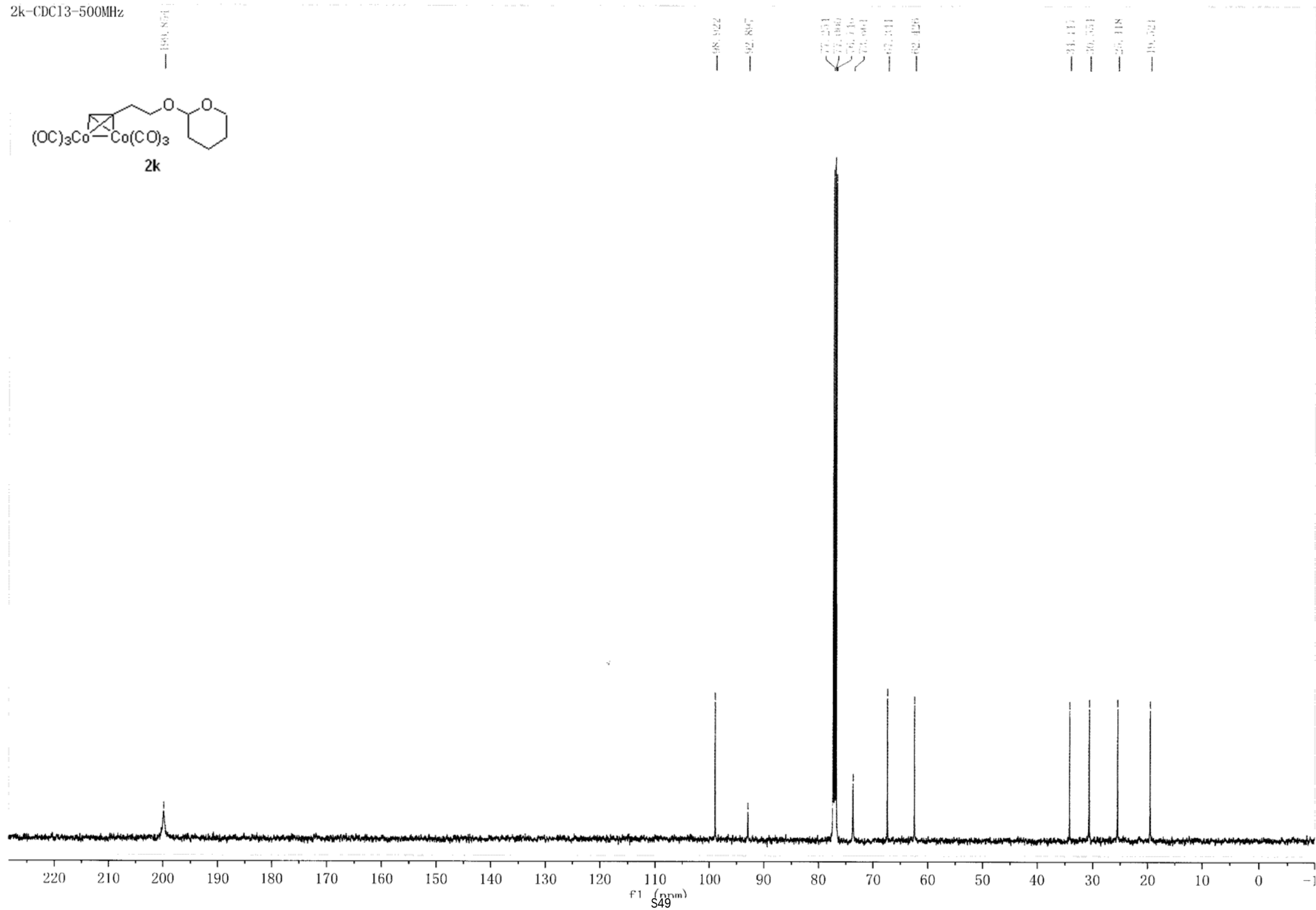
2k



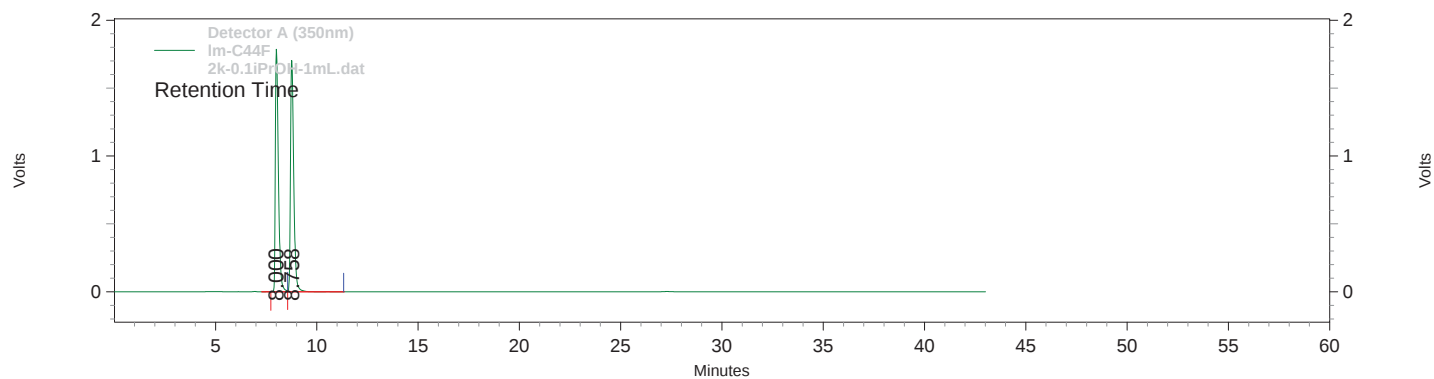
2k-CDC13-500MHz



2k



Method Name: C:\CLASS-VP\untitled.met
 Data Name: D:\CLASS-VP6.14\Data\Xu\2k-0.1iPrOH-1mL.dat
 User: System
 Acquired: 2016-12-15 11:19:56
 Printed: 2017-1-18 15:36:14

**Detector A (350nm)**

Pk #	Retention Time	Area	Area %	Height	Height %
1	8.000	18675391	49.498	1782030	51.208
2	8.758	19053910	50.502	1697976	48.792

Totals		37729302	100.000	3480005	100.000
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HPLC analysis of 2k

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Chiralpak-IB column

eluting solvent: 2-PrOH/n-hexane = 0.1:99.9

flow rate: 1 mL/min

column temperature: 25°C

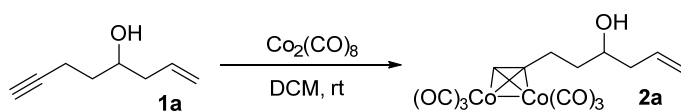
detection wavelength: 350 nm

.

retention factors: 1.500, 1.737

selective factor: 1.158

6. HPLC monitor of the reaction of **1a** and $\text{Co}_2(\text{CO})_8$



The next 3 pages are HPLC charts monitoring the reaction of **1a**, and $\text{Co}_2(\text{CO})_8$ in CH_2Cl_2 ,

HPLC conditions: CHIRALPAK-IB column, 0.4:99.6 *i*PrOH/*n*-hexane, $1 \text{ mL} \cdot \text{min}^{-1}$ flow rate, and 350 nm detection wavelength at 25°C .

Sample preparation: 20 μL of the reaction mixture was diluted with 0.5 mL *n*-hexane, passed through a disposable syringe filter (Nylon 66, 0.22 μm , 13 mm). 5 μL of the filtration was injected.

S52: $\text{Co}_2(\text{CO})_8$ in CH_2Cl_2 before addition of **1a**;

S53: 5 min after addition of **1a**;

S54: 1 h after addition of **1a**.

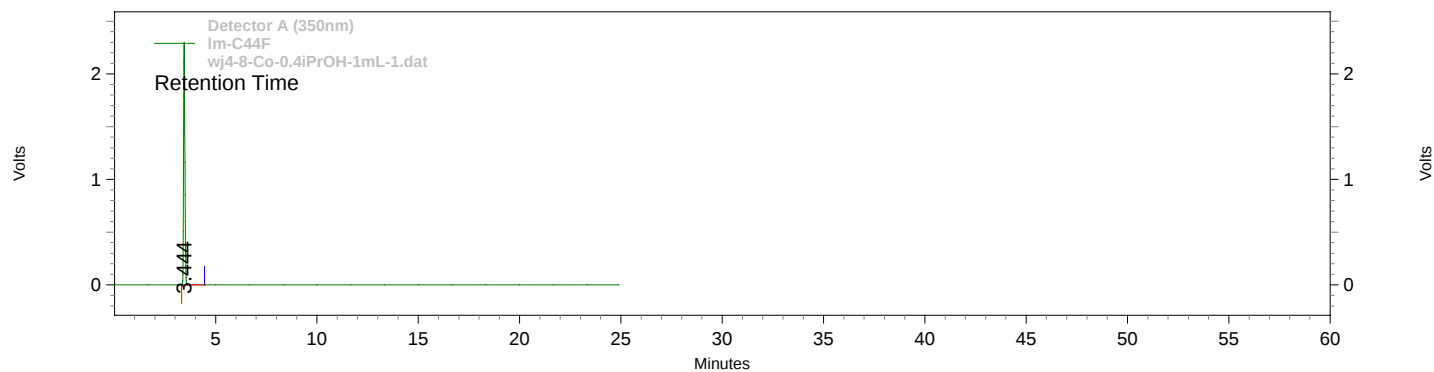
Method Name: C:\CLASS-VP\untitled.met

Data Name: D:\CLASS-VP6.14\Data\Xu\wj4-8-Co-0.4iPrOH-1mL-1.dat

User: System

Acquired: 2017-1-10 10:48:40

Printed: 2017-1-18 17:15:35

**Detector A (350nm)**

Pk #	Retention Time	Area	Area %	Height	Height %
1	3.444	10474869	100.000	2301258	100.000

Totals		10474869	100.000	2301258	100.000
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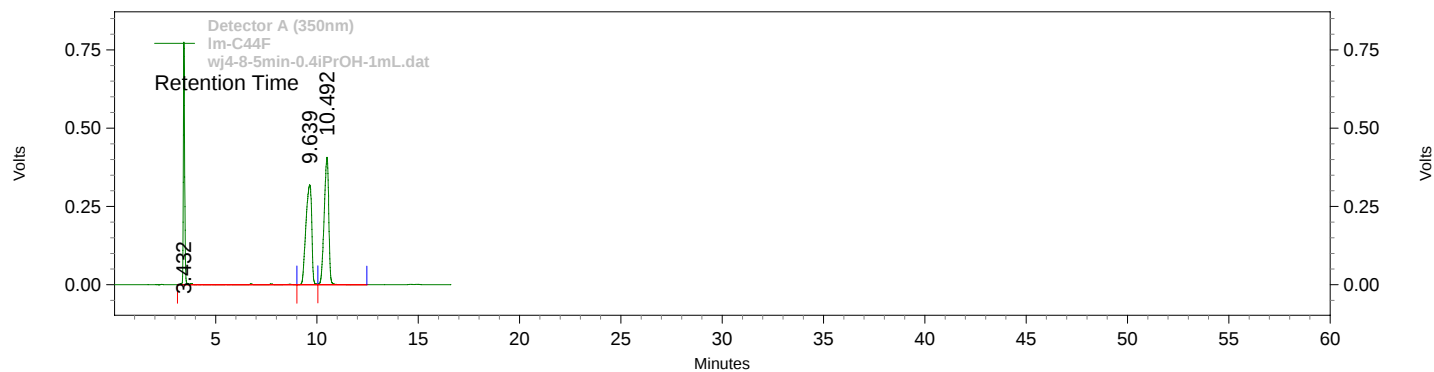
Method Name: C:\CLASS-VP\untitled.met

Data Name: D:\CLASS-VP6.14\Data\Xu\wj4-8-5min-0.4iPrOH-1mL.dat

User: System

Acquired: 2017-1-10 11:14:58

Printed: 2017-1-18 17:10:47

**Detector A (350nm)**

Pk #	Retention Time	Area	Area %	Height	Height %
1	3.432	3540718	21.784	774668	51.659
2	9.639	6341408	39.016	318152	21.216
3	10.492	6371285	39.200	406760	27.125

Totals		16253411	100.000	1499580	100.000
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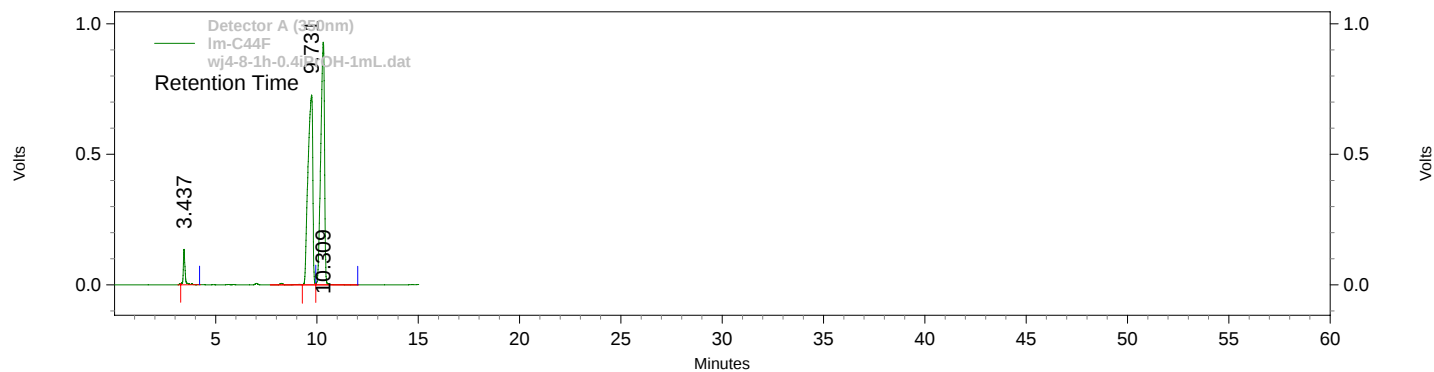
Method Name: C:\CLASS-VP\untitled.met

Data Name: D:\CLASS-VP6.14\Data\Xu\wj4-8-1h-0.4iPrOH-1mL.dat

User: System

Acquired: 2017-1-10 12:19:05

Printed: 2017-1-18 17:14:35

**Detector A (350nm)**

Pk #	Retention Time	Area	Area %	Height	Height %
1	3.437	796748	3.230	136158	7.596
2	9.731	11919039	48.317	726707	40.543
3	10.309	11952799	48.454	929573	51.861

Totals		24668586	100.000	1792438	100.000
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