Supporting information

μ-Hydroxyl Trinuclear Copper(II) Cluster: Reactivity and Unusual Formation in Three-Component Synthesis of 1,2,3-Triazoles in Aqueous Media

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1. UV-vis spectra of Cu-1 and Cu-6

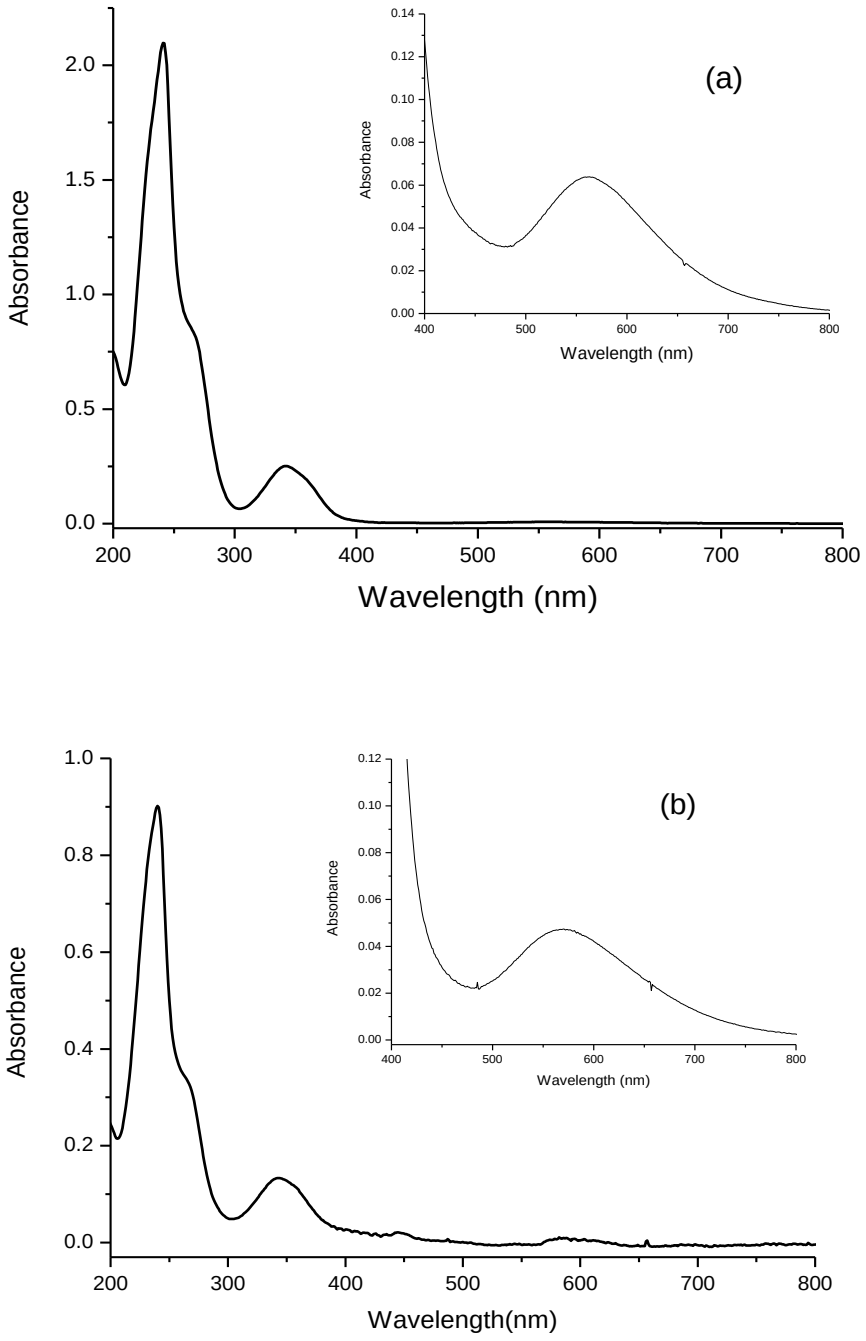


Figure S1. UV-vis spectra of (a) μ-O(H) trinuclear copper(II) cluster (**Cu-6**) in aqueous solution with a concentration of 2.29×10^{-5} mol/L. Inset: A expanded spectra from 400 nm to 800, with a concentration of 2.29×10^{-4} mol/L. The λ_{max}/nm (ε/$M^{-1}\bullet cm^{-1}$) are 242 (91500), 270 (sh), 343 (10950), 564 (285); and (b) **Cu-1** in aqueous solution. Inset: A expanded spectra from 400 nm to 800, with a concentration of 3.15×10^{-4} mol/L. The ε at 564 nm is 149 $M^{-1}\bullet cm^{-1}$.

2. Characterizations of μ-O(H) trinuclear copper(II) cluster (Cu-6): ESI-MS (negative) and FTIR spectra

μ-O(H) trinuclear copper(II) cluster (Cu-6)

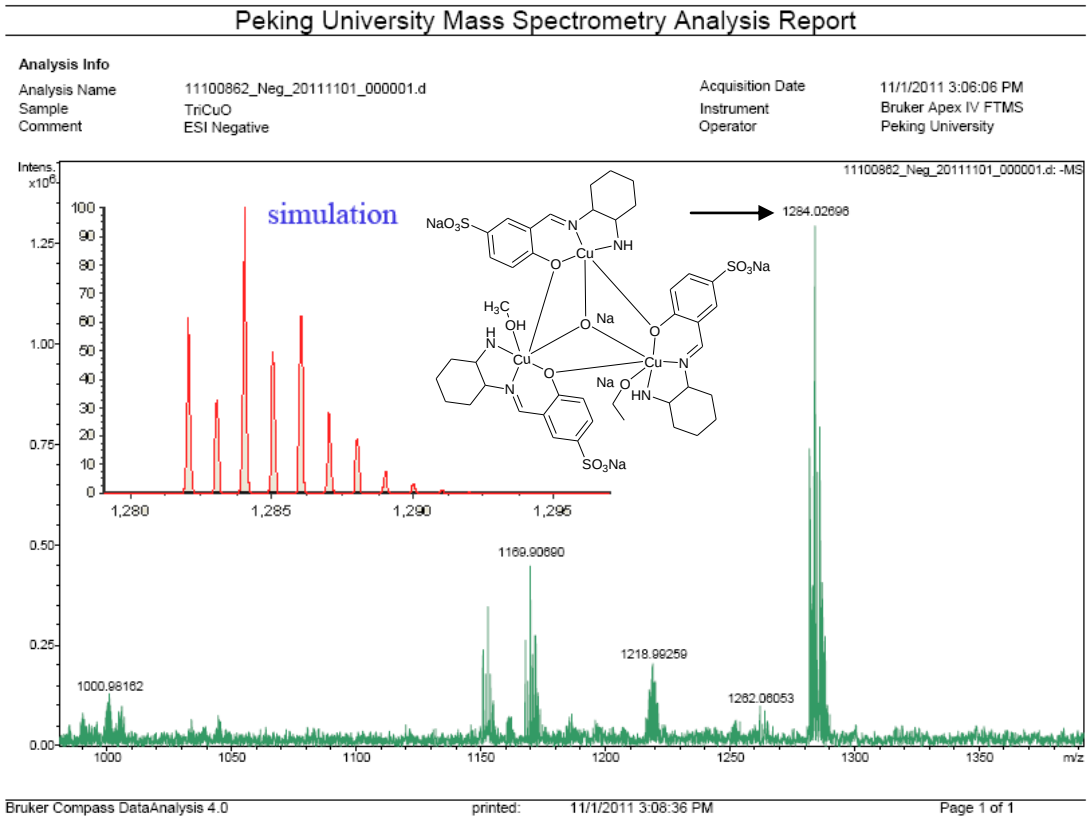


Figure S2 ESI-MS (negative) spectra of μ-O(H) trinuclear copper(II) cluster (**Cu-6**). Insert are the structure and simulated spectrum.

FTIR spectrum of μ-O(H) trinuclear copper(II) cluster (Cu-6)

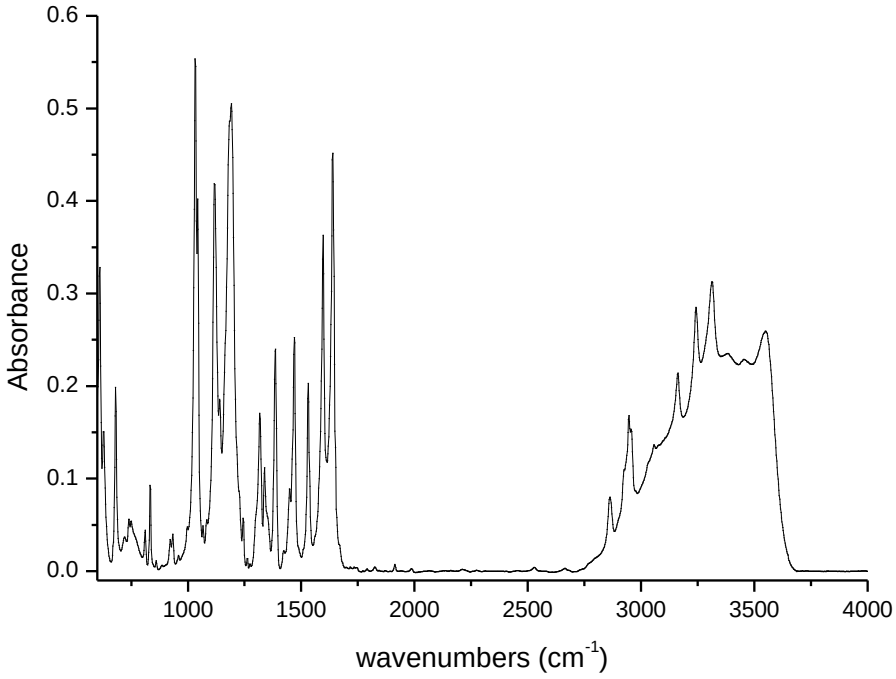


Figure S3. FTIR spectrum of μ-O(H) trinuclear copper(II) cluster (**Cu-6**). (KBr)

3. UV-vis spectra of trinuclear copper(II) cluster Cu-7

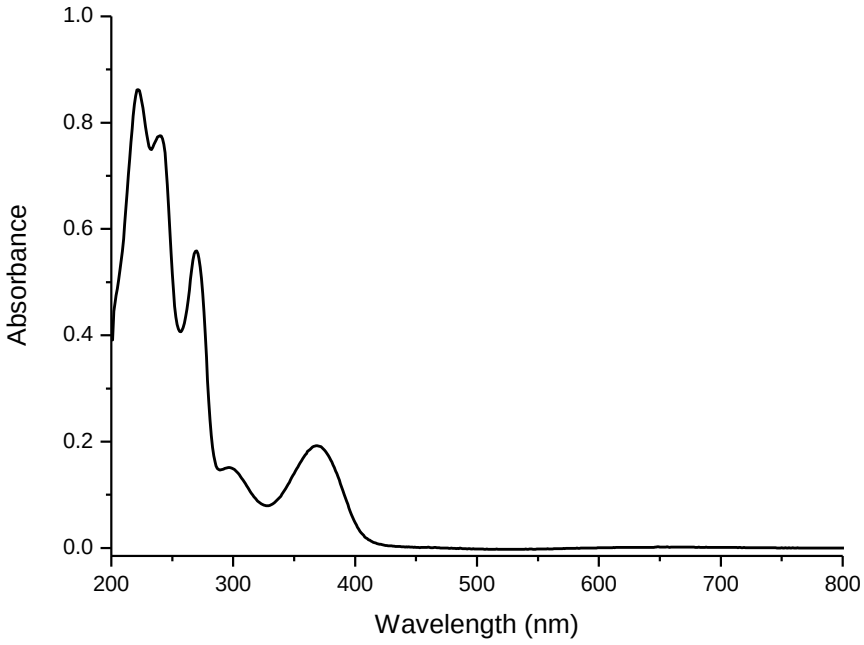


Figure S4. UV-vis spectra of nuclear copper(II) cluster **Cu-7** in methanol.

4. GC detection of *β*-hydroxy benzyl azide

Gas chromatography was performed on an Agilent 7890A gas chromatography with FID detector, using a 30 m×0.25 mm^2 Chiral G-TA capillary column.

Sample preparations: Cu-1 (0.03 mmol), NaN_3 (0.5 mmol), and styrene epoxide (0.5 mmol) was added to water (10 mL) and stirred at room temperature overnight. 1 mL of the suspension was extracted by ethyl acetate. Then 25 μL chlorobenzene was added as an internal standard. The solution was dried by anhydrous Na_2SO_4 and used for GC experiments.

GC conditions for measuring the enantiomers of *β*-hydroxy benzyl azide:
Inlet temperature: 250 ^oC
No split.
Step 1: 50 ^oC for 1 min.
Step 2: 70 ^oC for 10 min.
Step 3: 180 ^oC for 5 min.
Flow: 3.9 mL/min

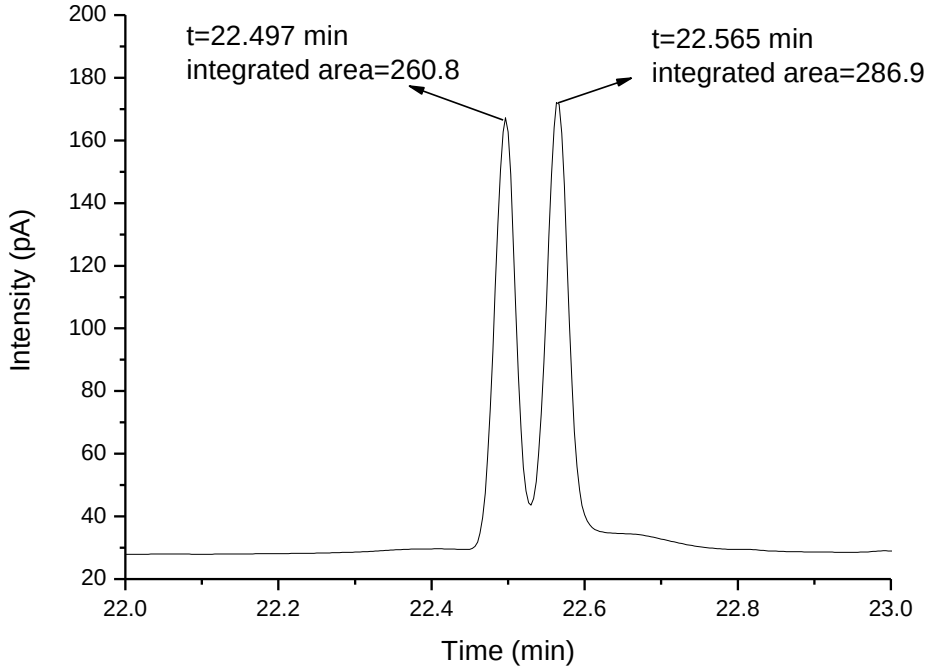


Figure S5. GC curve for *β*-hydroxy benzyl azide, the product of styrene epoxide and NaN_3 in aqueous solution in the presence of catalyst **Cu-1**. The integrated areas of two enantiomers are quite similar, which indicates that there is no enantiomeric excess for the products.

5. Crystal data and structure refinement for Cu-1.

Identification code	**Cu-1**
Empirical formula	C20 H29 Cu N2 Na2 O14.50 S2
Formula weight	703.09
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.8998(4) A alpha = 103.382(4) deg. b = 11.5756(7) A beta = 94.177(4) deg. c = 16.6900(9) A gamma = 103.844(4) deg.
Volume	1428.30(14) A^3
Z, Calculated density	2, 1.635 Mg/m^3
Absorption coefficient	1.013 mm^-1
F(000)	724
Crystal size	0.10 x 0.06 x 0.04 mm
Theta range for data collection	2.52 to 27.75 deg.
Limiting indices	-10<=h<=10, -14<=k<=15, -21<=l<=21
Reflections collected / unique	12691 / 6590 [R(int) = 0.0460]
Completeness to theta = 27.75	97.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8067 and 0.4012
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6590 / 0 / 436
Goodness-of-fit on F^2	1.121
Final R indices [I>2sigma(I)]	R1 = 0.0762, wR2 = 0.2168
R indices (all data)	R1 = 0.0960, wR2 = 0.2273
Largest diff. peak and hole	1.500 and -0.758 e.A^-3

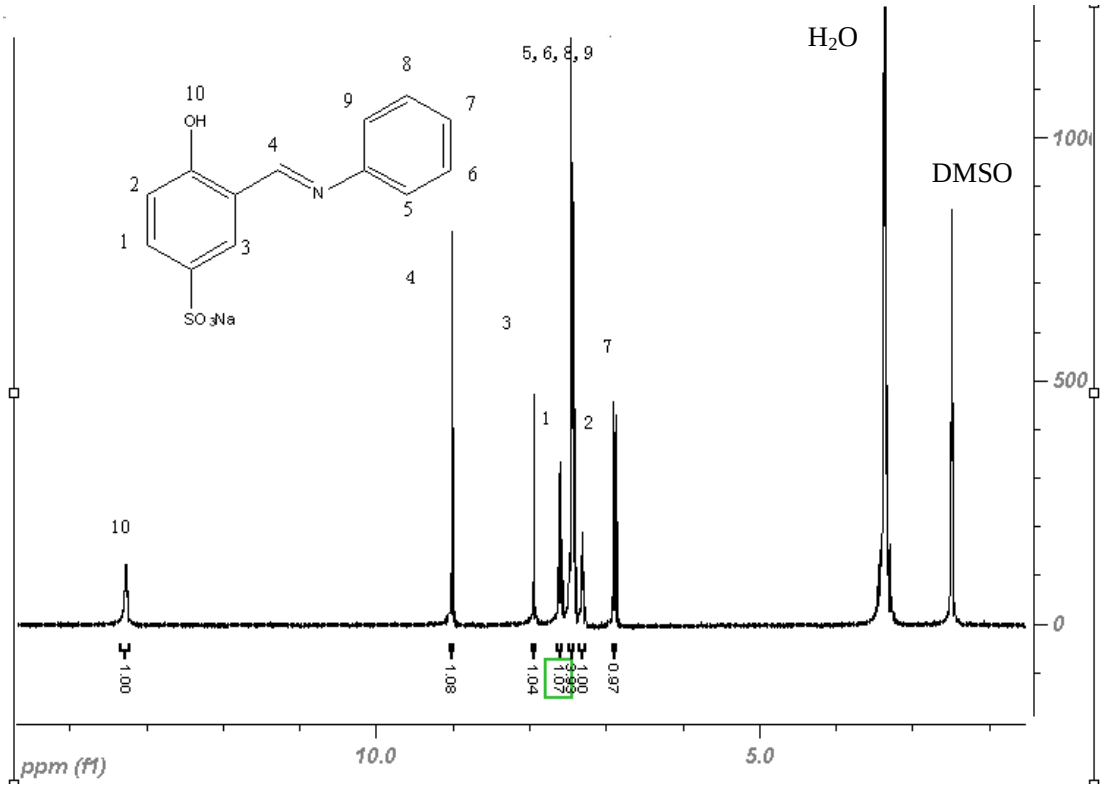
Crystal data and structure refinement for Cu-5.

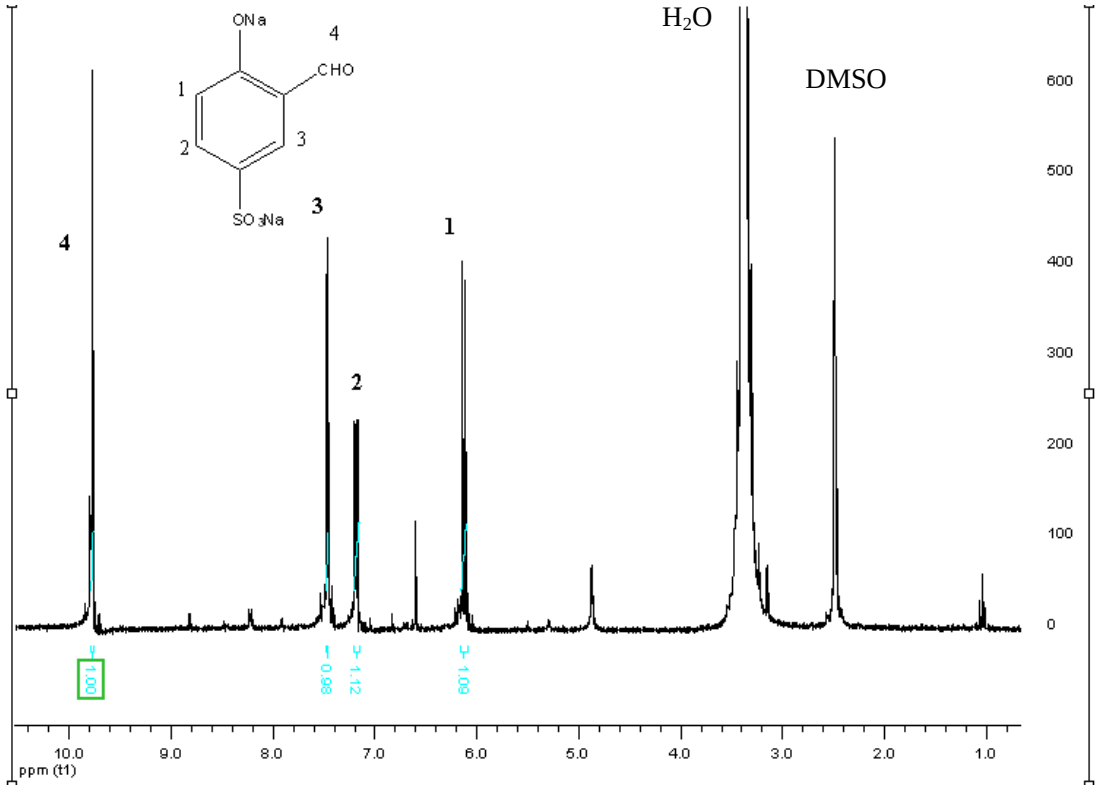
Identification code	**Cu-5**
Empirical formula	C13 H22 Cu N2 O7 S
Formula weight	413.93
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.4021(13) A alpha = 65.210(2) deg. b = 9.6265(13) A beta = 76.389(2) deg. c = 10.5993(14) A gamma = 73.383(2) deg.
Volume	827.18(19) A^3
Z, Calculated density	2, 1.662 Mg/m^3
Absorption coefficient	1.485 mm^-1
F(000)	430
Crystal size	0.20 x 0.18 x 0.10 mm
Theta range for data collection	2.28 to 27.58 deg.
Limiting indices	-12<=h<=11, -12<=k<=11, -13<=l<=13
Reflections collected / unique	4890 / 3650 [R(int) = 0.0138]
Completeness to theta = 27.58	95.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8657 and 0.7555
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3650 / 6 / 286
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 = 0.0837
R indices (all data)	R1 = 0.0391, wR2 = 0.0872
Largest diff. peak and hole	0.502 and -0.368 e.A^-3

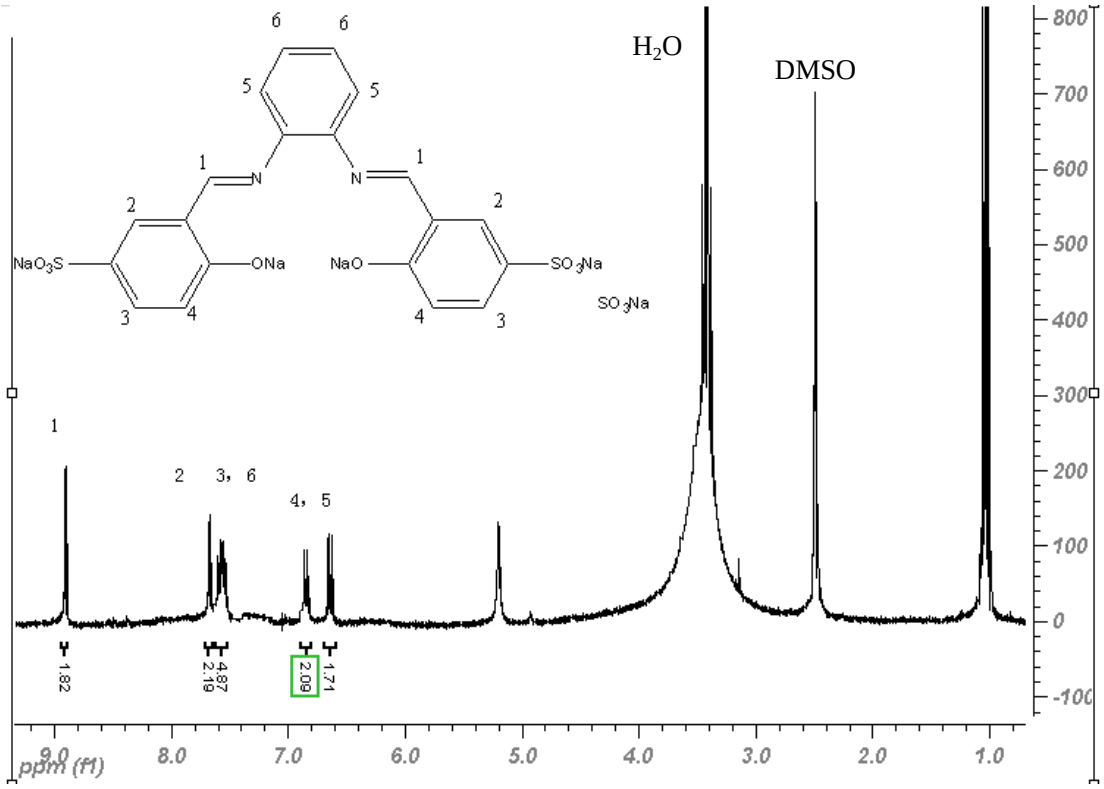
Crystal data and structure refinement for Cu-6.

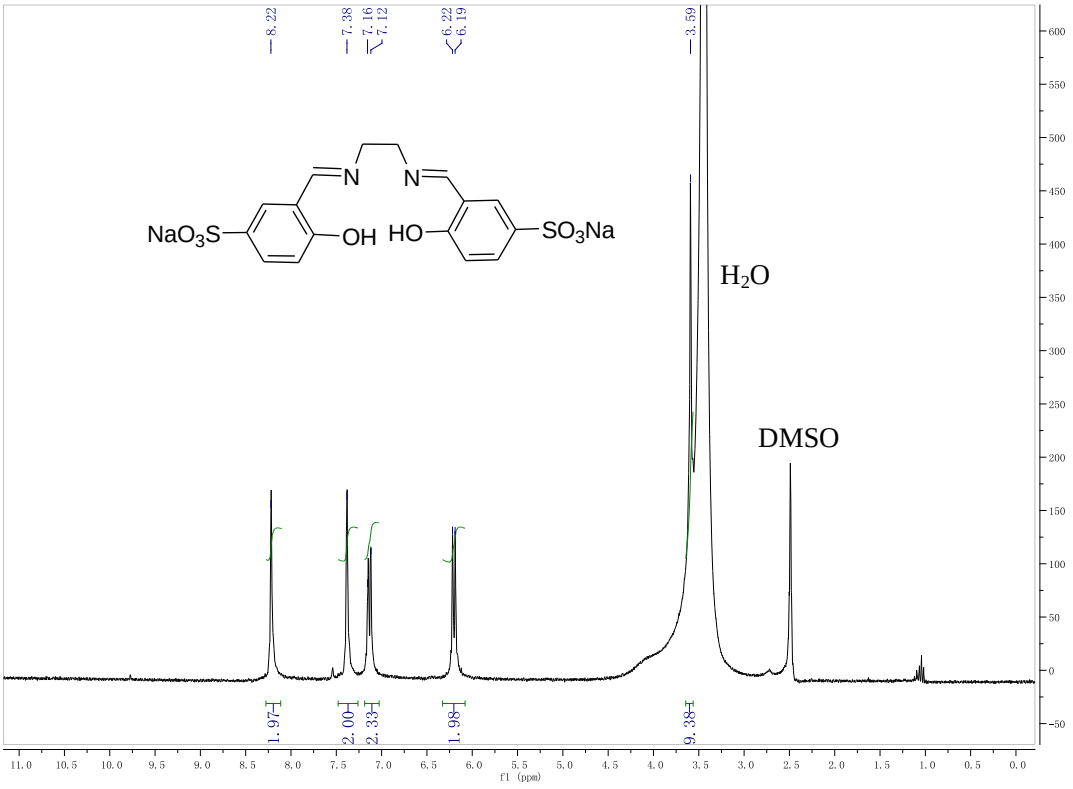
Identification code	**Cu-6**
Empirical formula	C41 H66 Cu3 N6 O19 S3
Formula weight	1233.80
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Trigonal, P3(1)
Unit cell dimensions	a = 14.083(2) A alpha = 90 deg. b = 14.083(2) A beta = 90 deg. c = 23.118(5) A gamma = 120 deg.
Volume	3970.4(11) A^3
Z, Calculated density	3, 1.548 Mg/m^3
Absorption coefficient	1.389 mm^-1
F(000)	1923
Crystal size	0.15 x 0.13 x 0.10 mm
Theta range for data collection	1.89 to 27.62 deg.
Limiting indices	-13<=h<=18, -18<=k<=13, -26<=l<=29
Reflections collected / unique	23778 / 11017 [R(int) = 0.0286]
Completeness to theta = 27.62	99.4 %
Absorption correction	None
Max. and min. transmission	0.8187 and 0.7996
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11017 / 2 / 654
Goodness-of-fit on F^2	0.969
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0970
R indices (all data)	R1 = 0.0525, wR2 = 0.1046
Absolute structure parameter	0.032(10)
Largest diff. peak and hole	0.746 and -0.579 e.A^-3

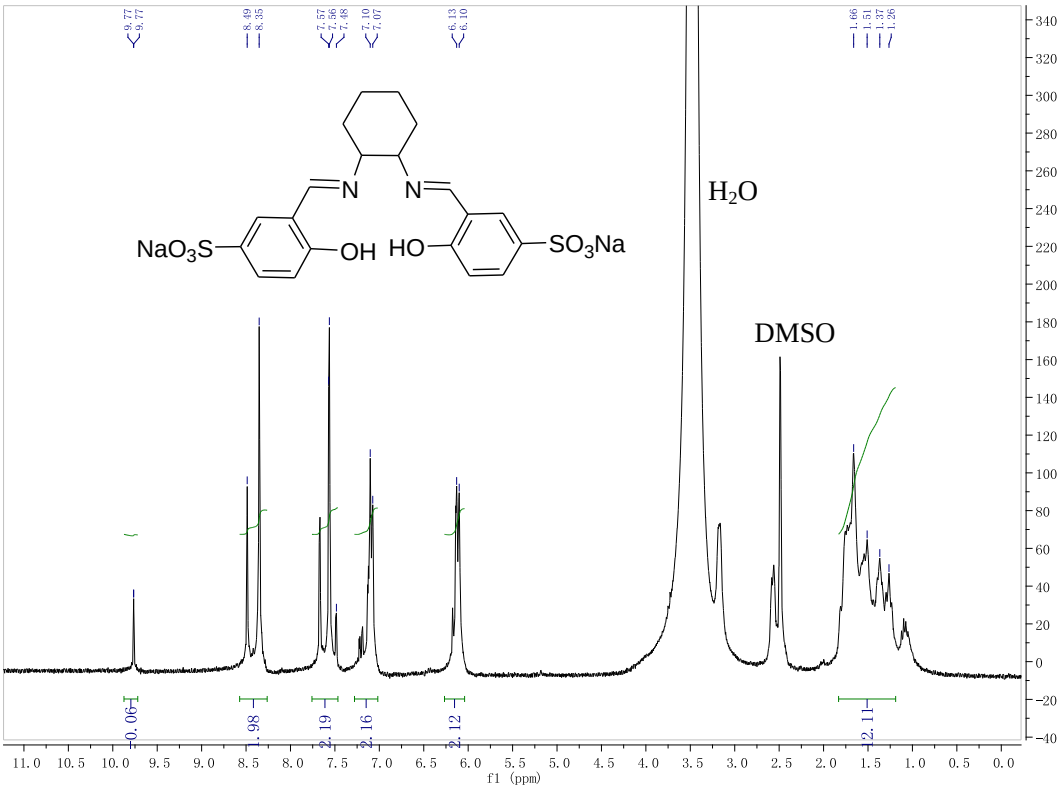
6. NMR spectra of catalysts and products

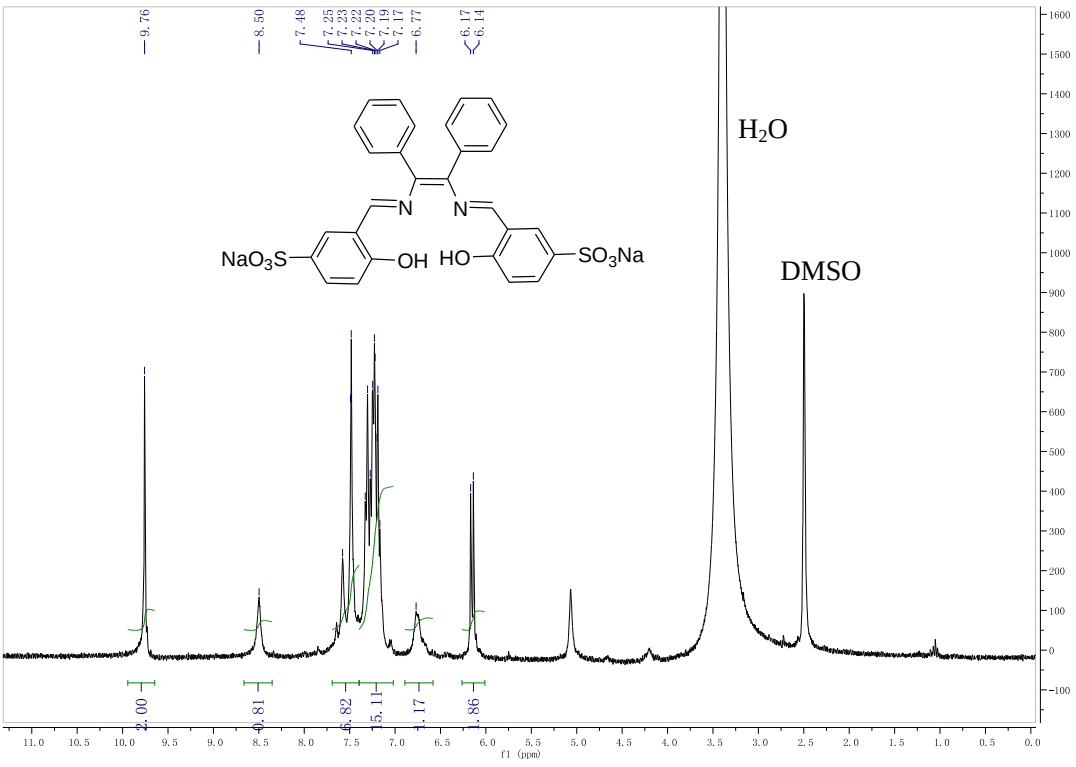





H2O
DMSO
NaO3S
ONa
NaO
SO3Na
SO3Na
1
2 3, 6
4, 5
1.82
4.87
2.19
2.09
1.71
ppm (f1)


8.22
7.38
7.16
7.12
6.22
6.19
3.59
NaO3S
OH
HO
SO3Na
H2O
DMSO
1.97
2.00
2.33
1.98
9.38
f1 (ppm)


9.77
9.77
8.49
8.35
7.57
7.56
7.48
7.10
7.07
6.13
6.10
1.66
1.51
1.37
1.26
N
N
NaO3S
OH
HO
SO3Na
H2O
DMSO
0.06
1.98
2.19
2.16
2.12
12.11
f1 (ppm)


9.76
8.50
7.48
7.25
7.23
7.22
7.20
7.19
7.17
6.77
6.17
6.14
N
N
NaO3S
OH
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SO3Na
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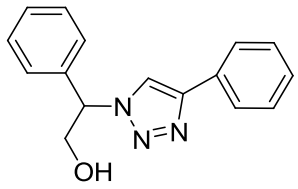
DMSO
2.00
0.81
6.82
15.11
3.17
1.86
f1 (ppm)



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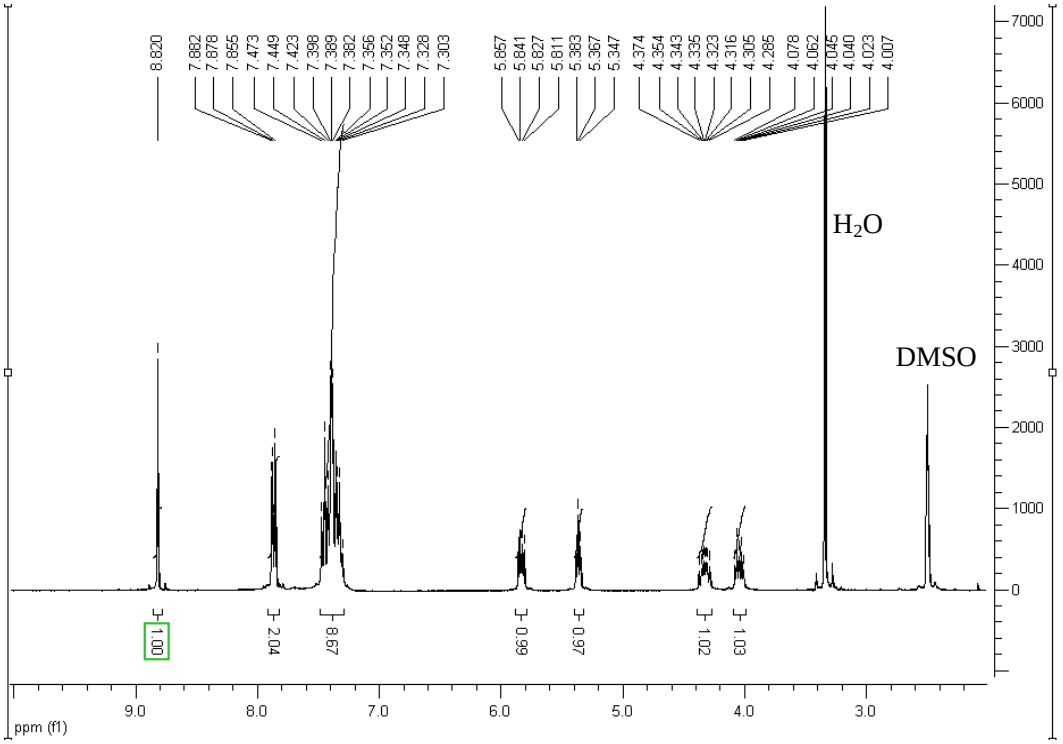
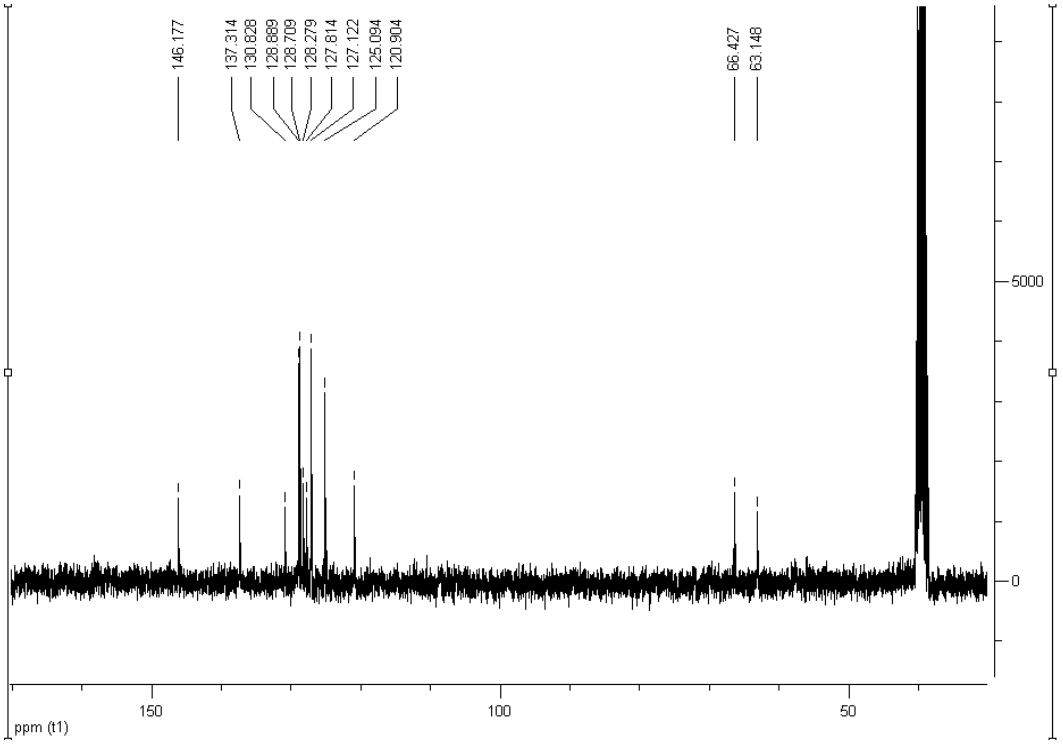
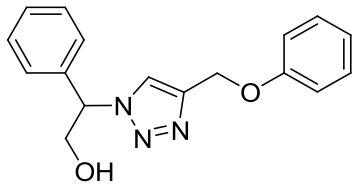




The above spectra is ^{1}H NMR, and the below spectra is ^{13}C NMR



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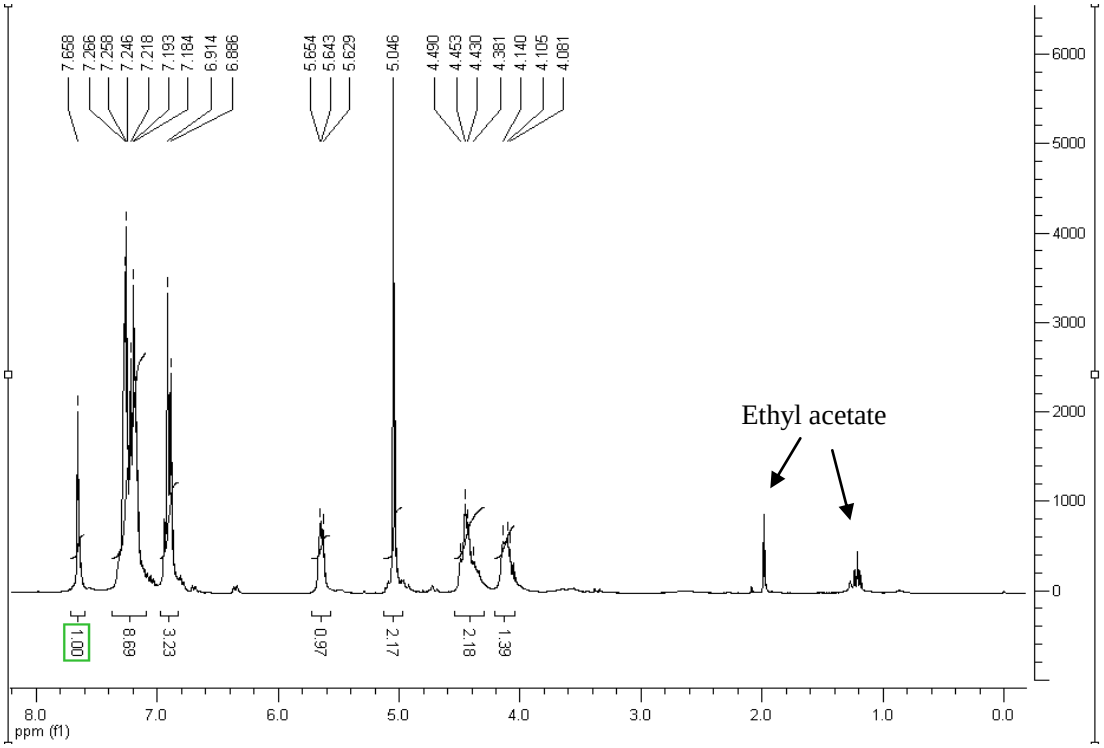

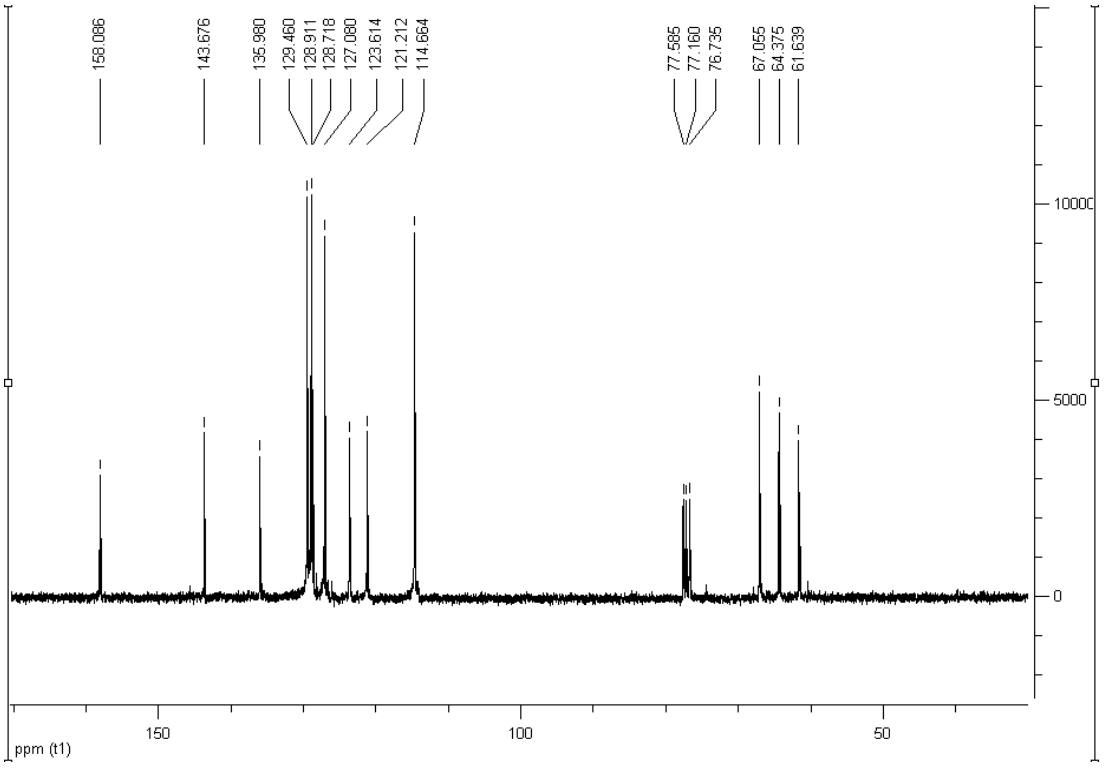

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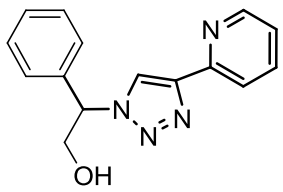

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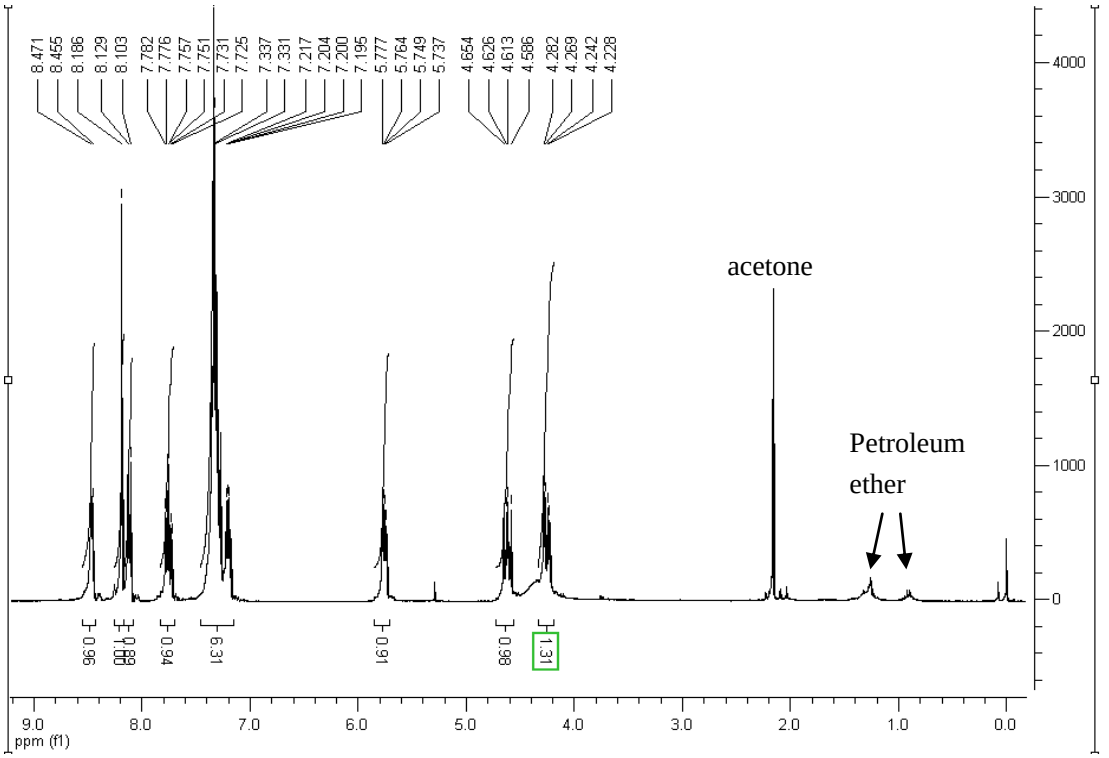
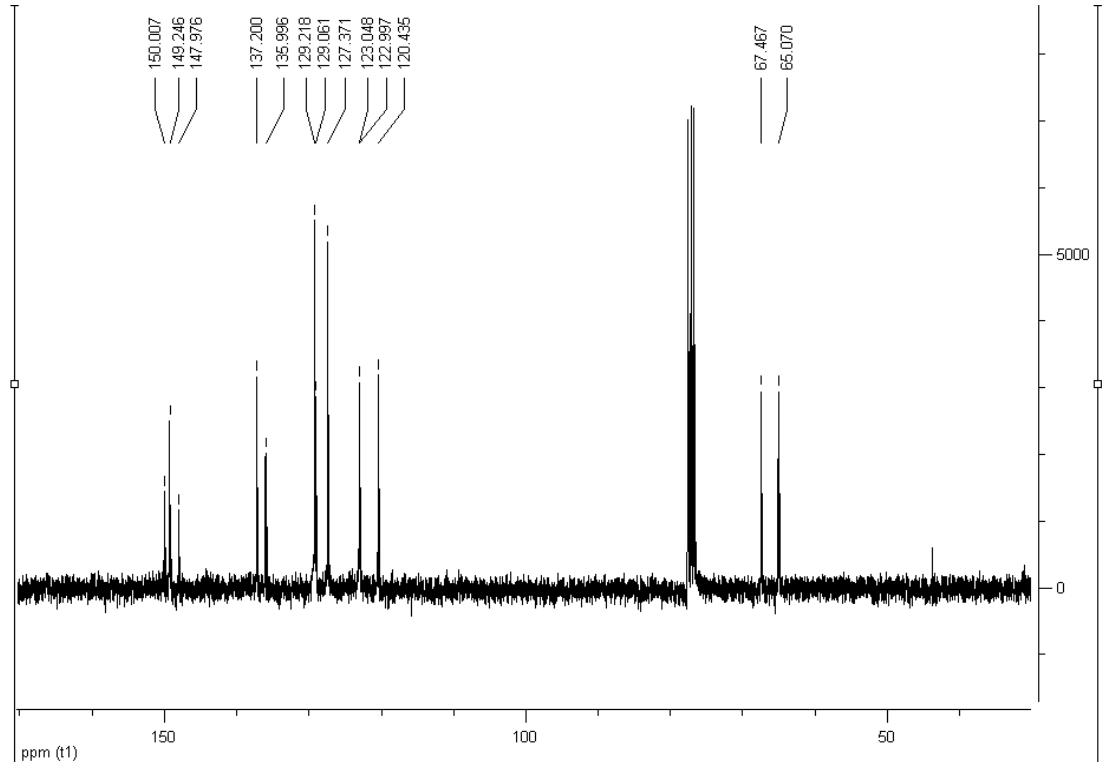
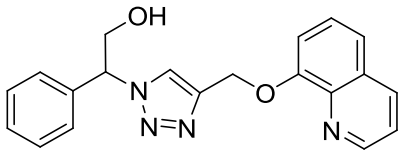




The above spectra is ^{1}H NMR, and the below spectra is ^{13}C NMR



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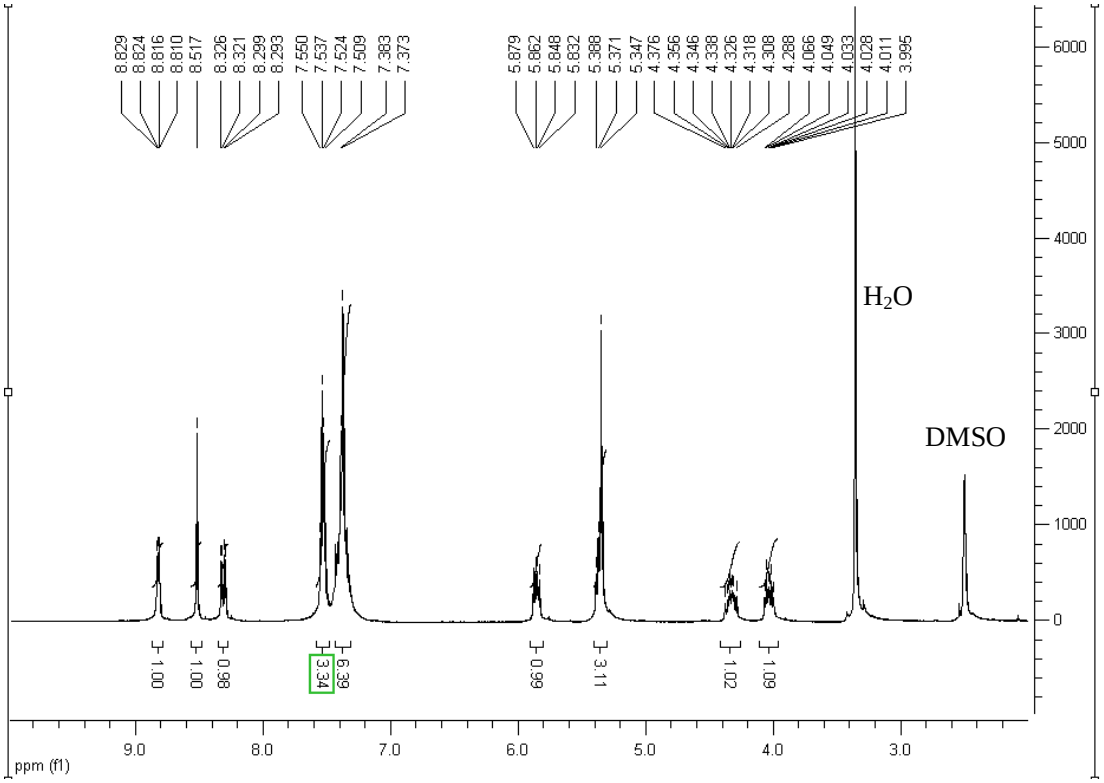

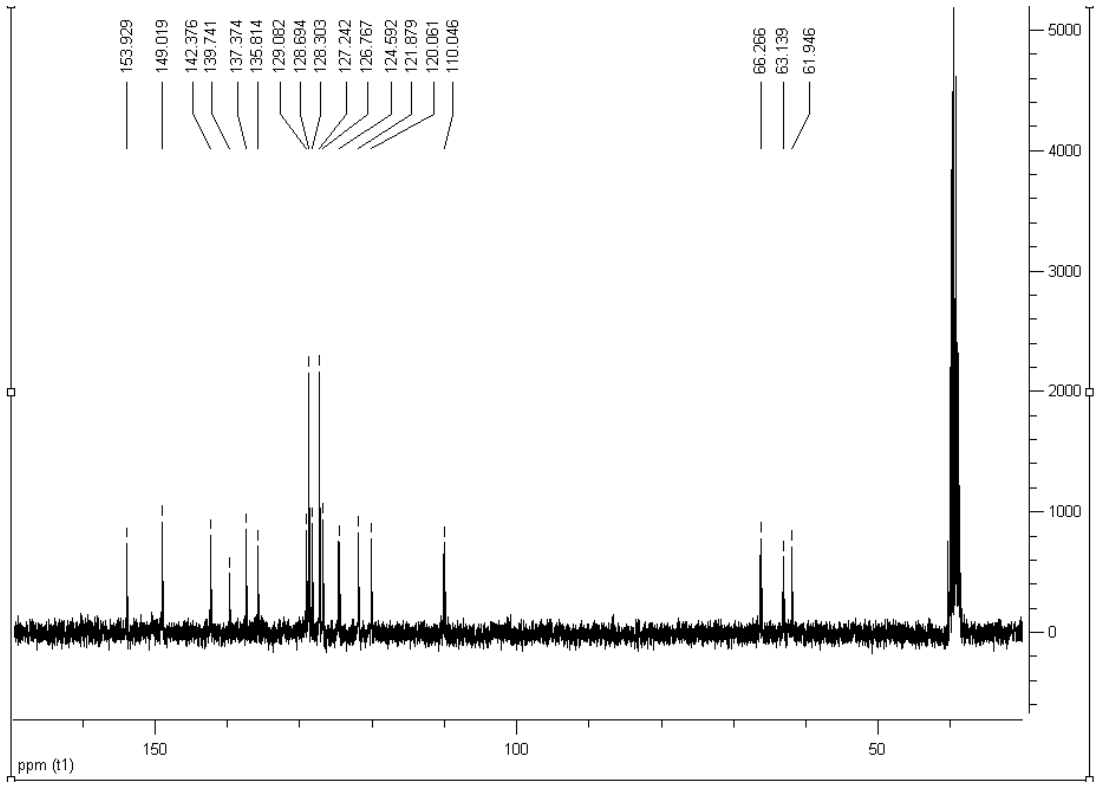

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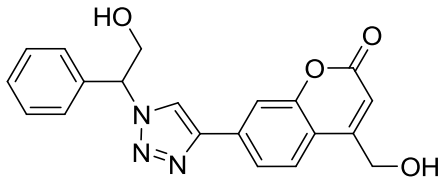

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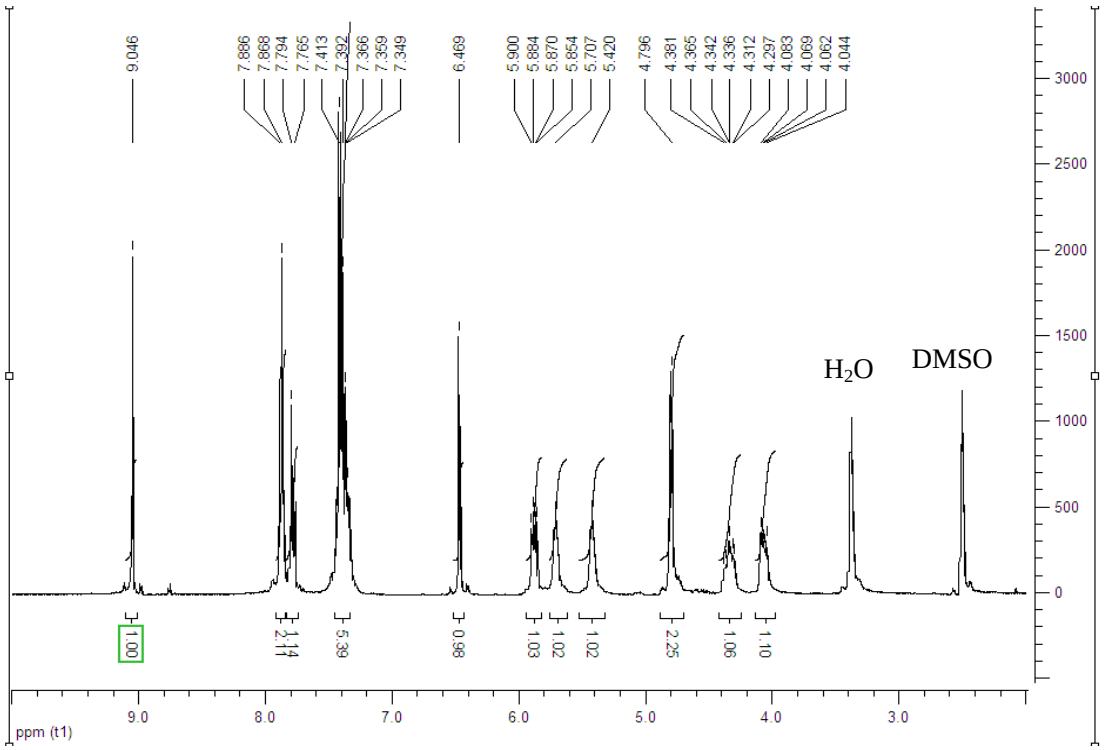

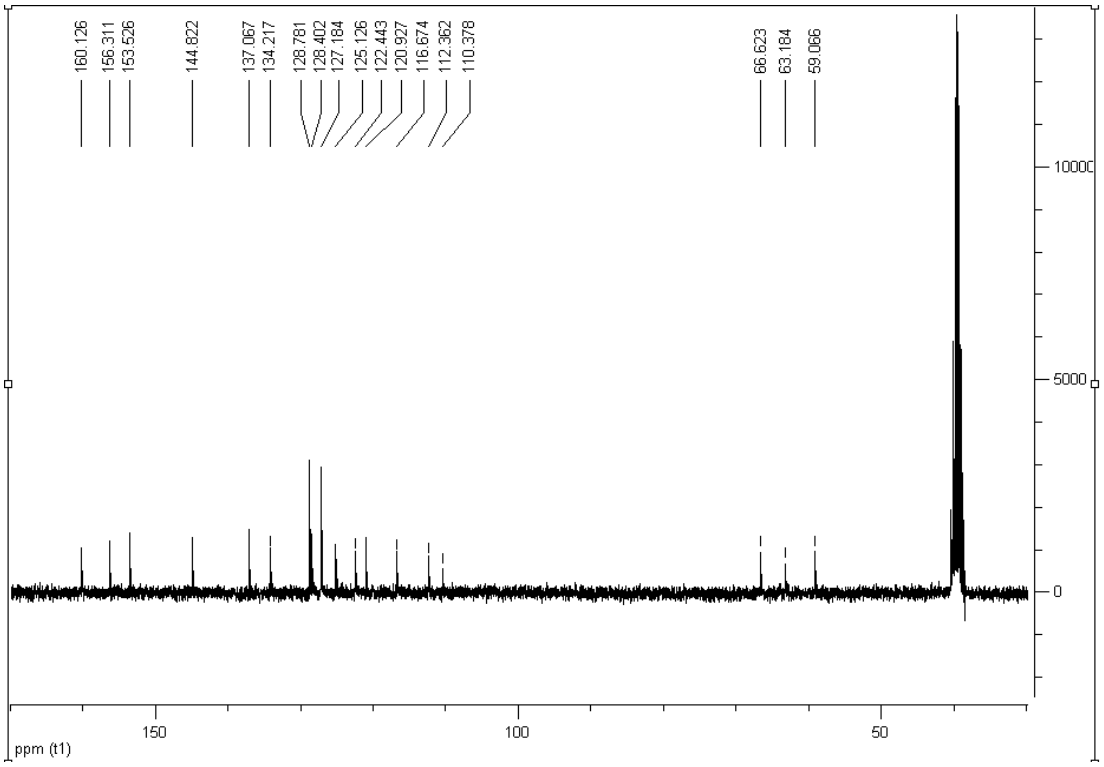

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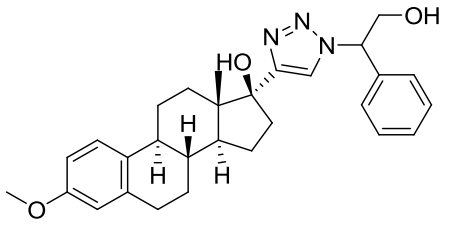

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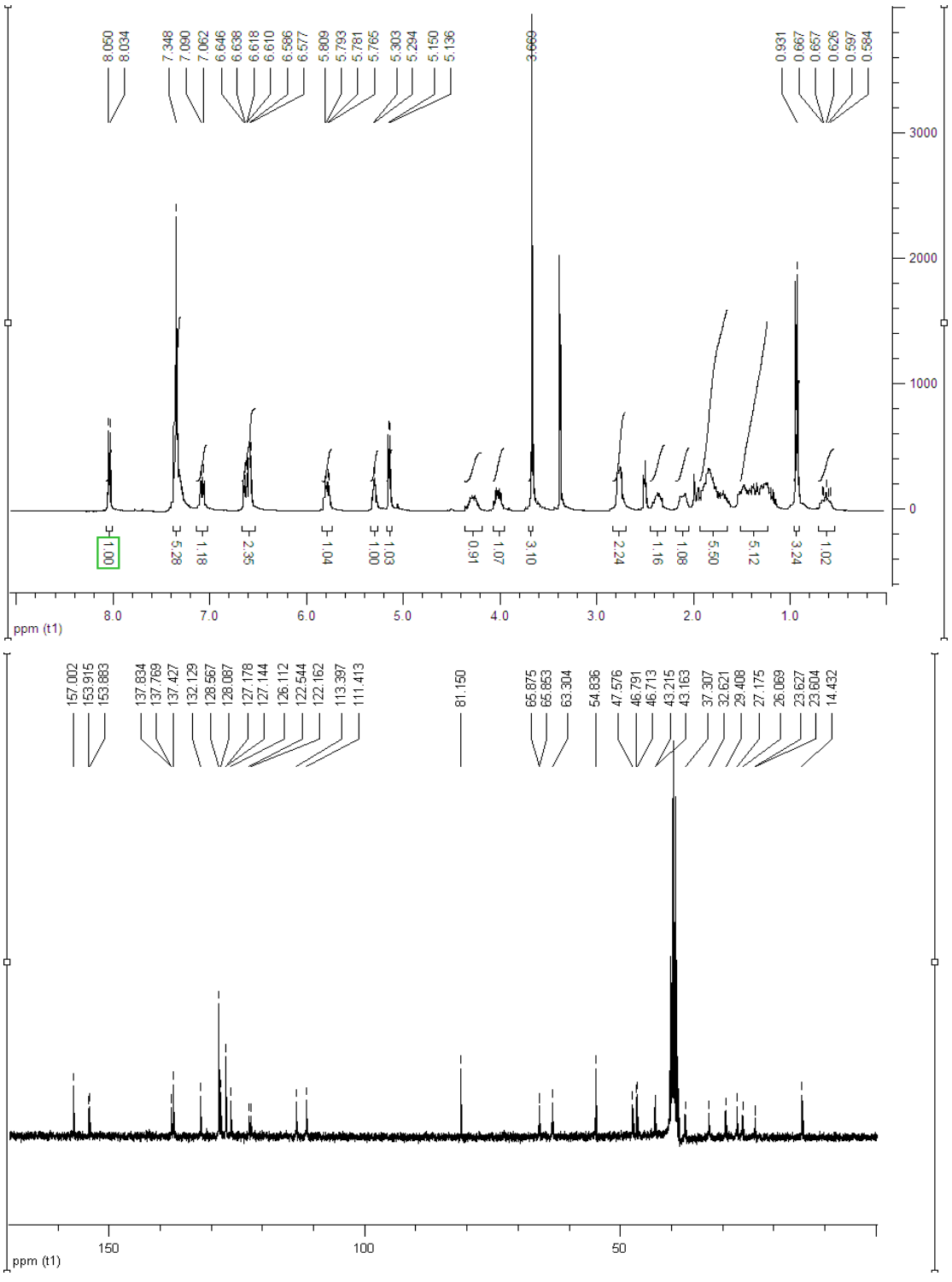

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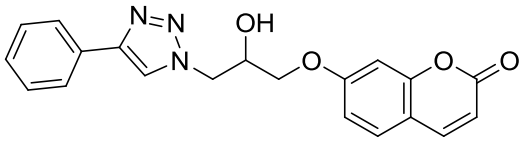

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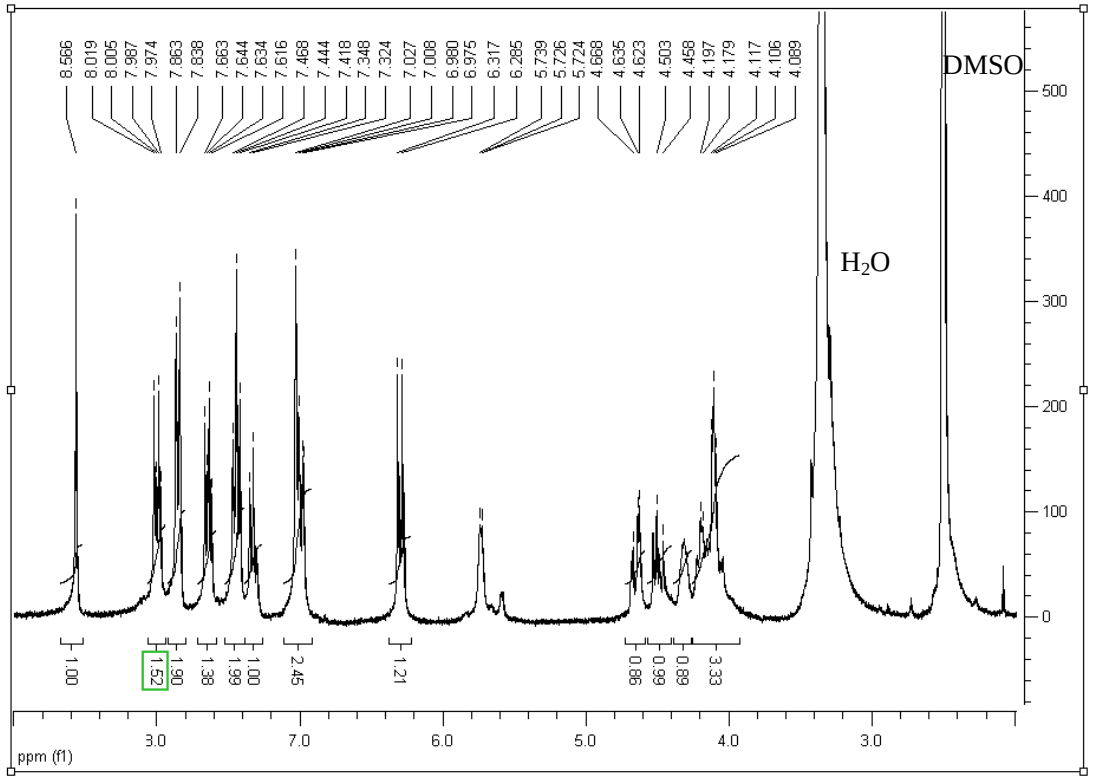
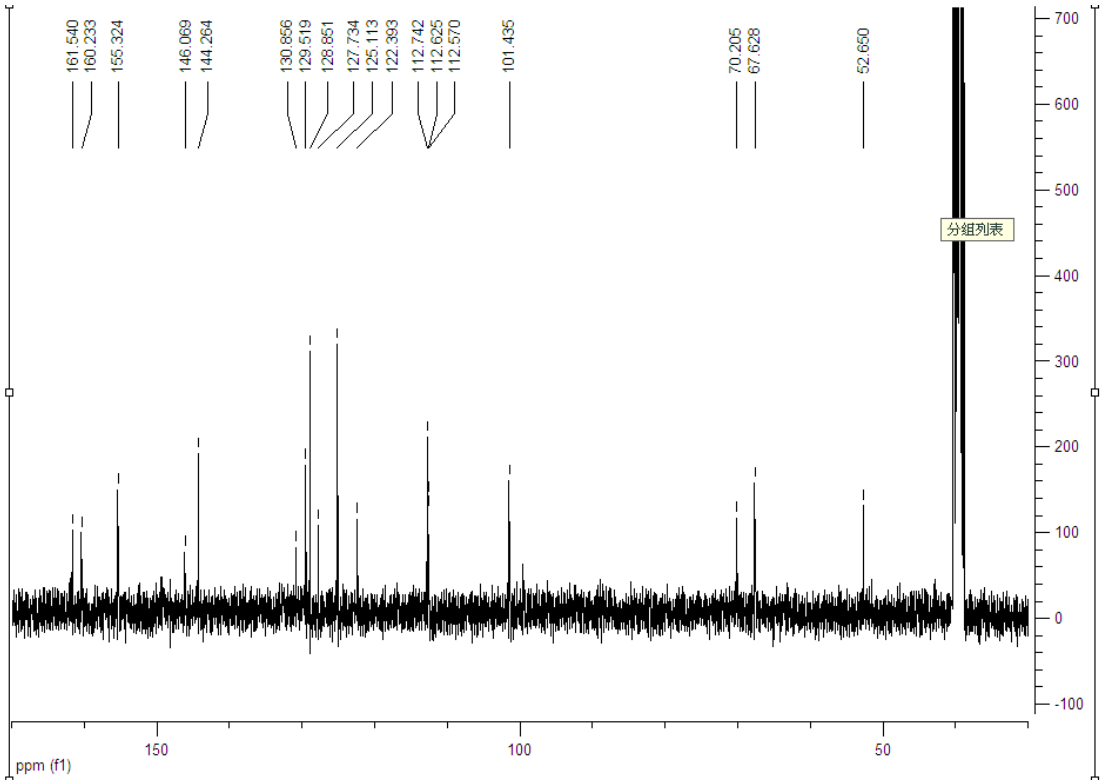
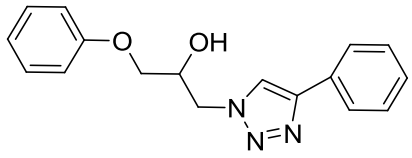




The above spectra is ^{1}H NMR, and the below spectra is ^{13}C NMR



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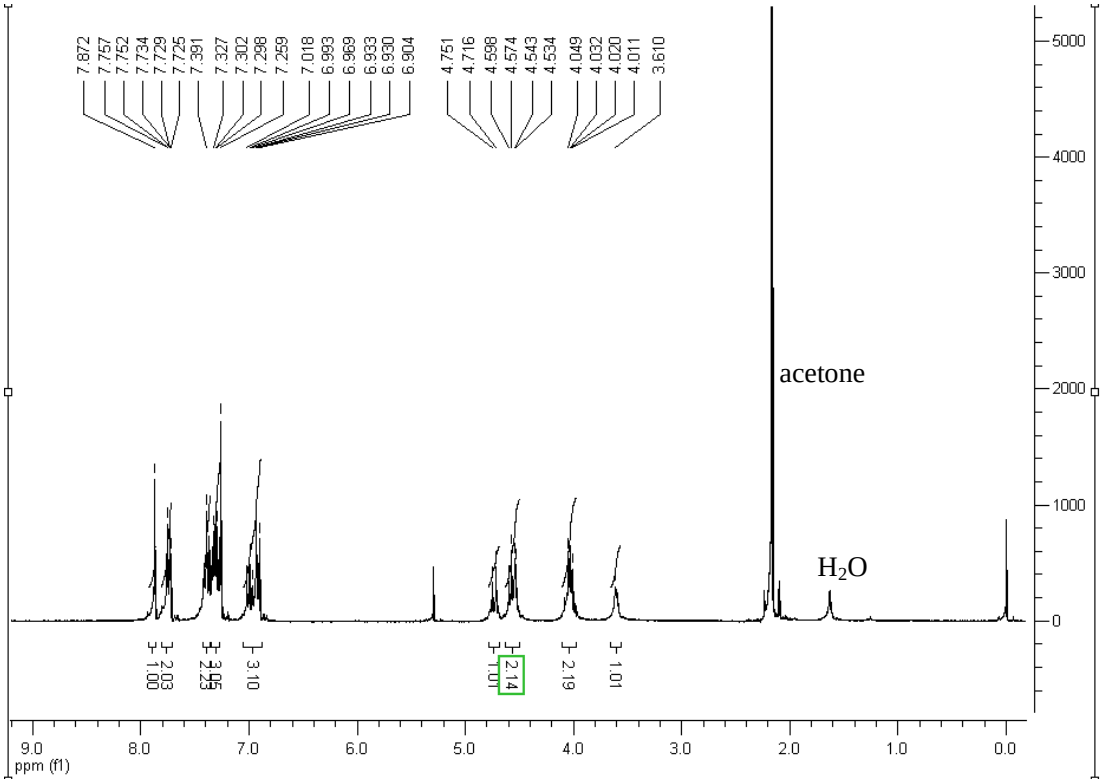
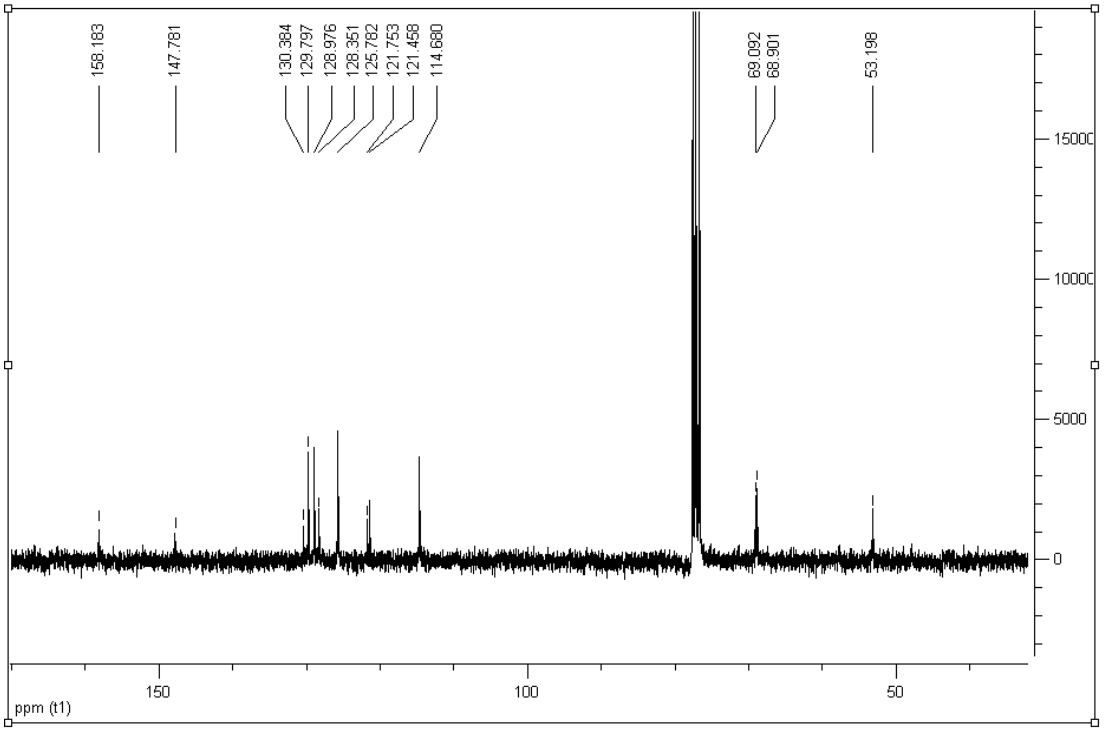
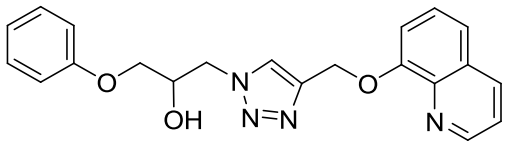




The above spectra is ^{1}H NMR, and the below spectra is ^{13}C NMR



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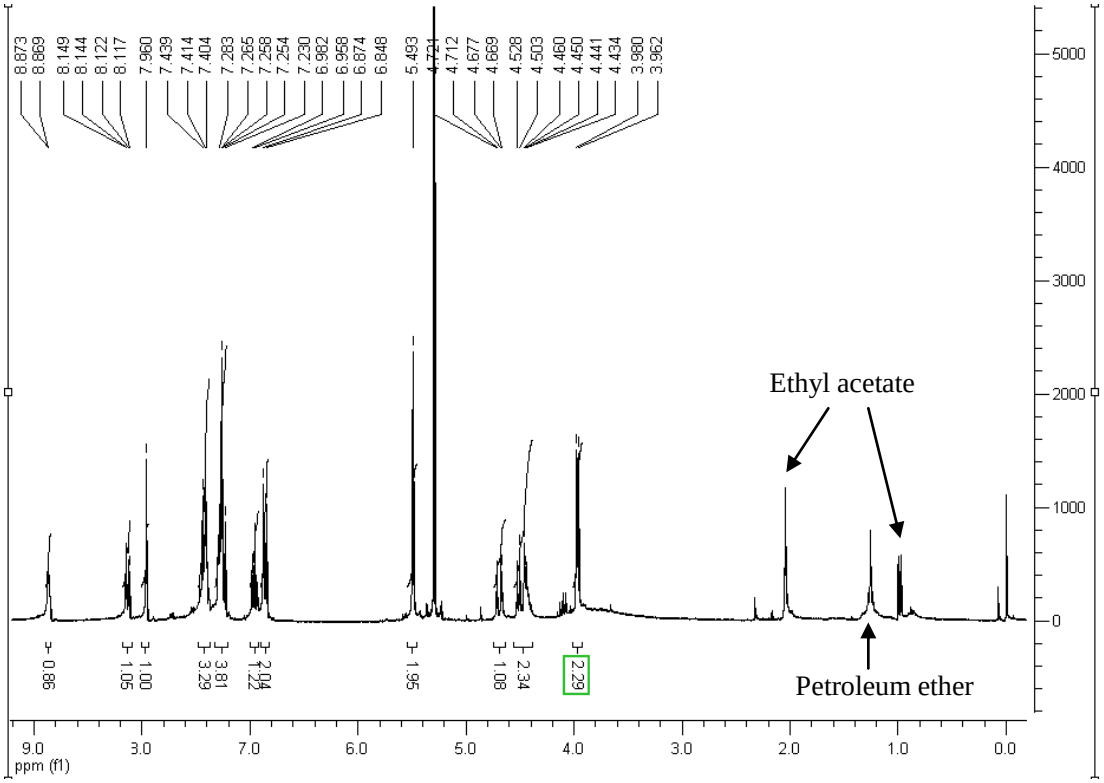
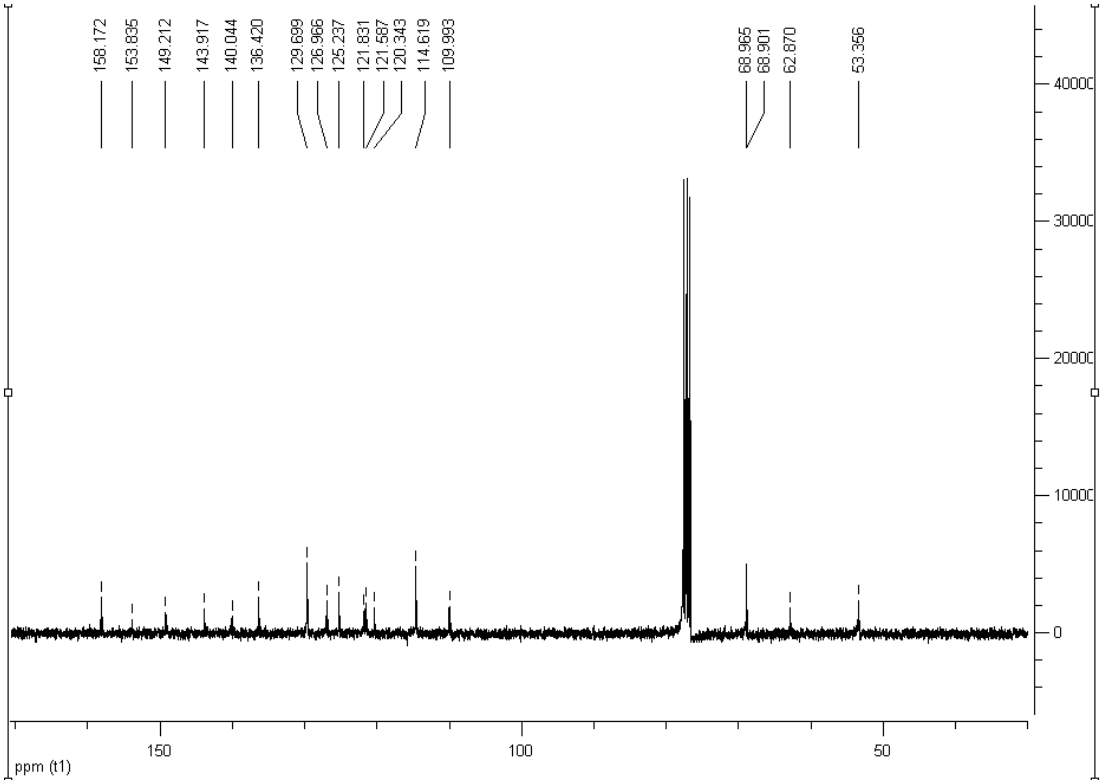
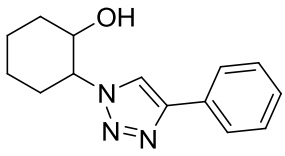




The above spectra is ^{1}H NMR, and the below spectra is ^{13}C NMR



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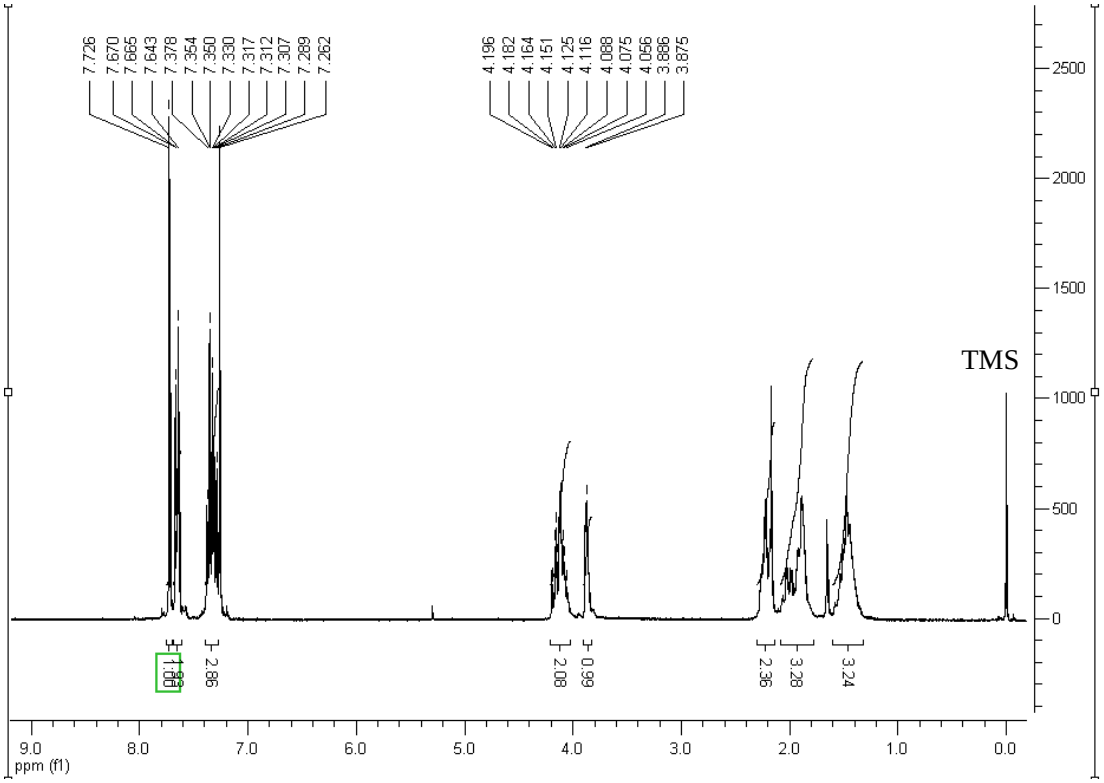
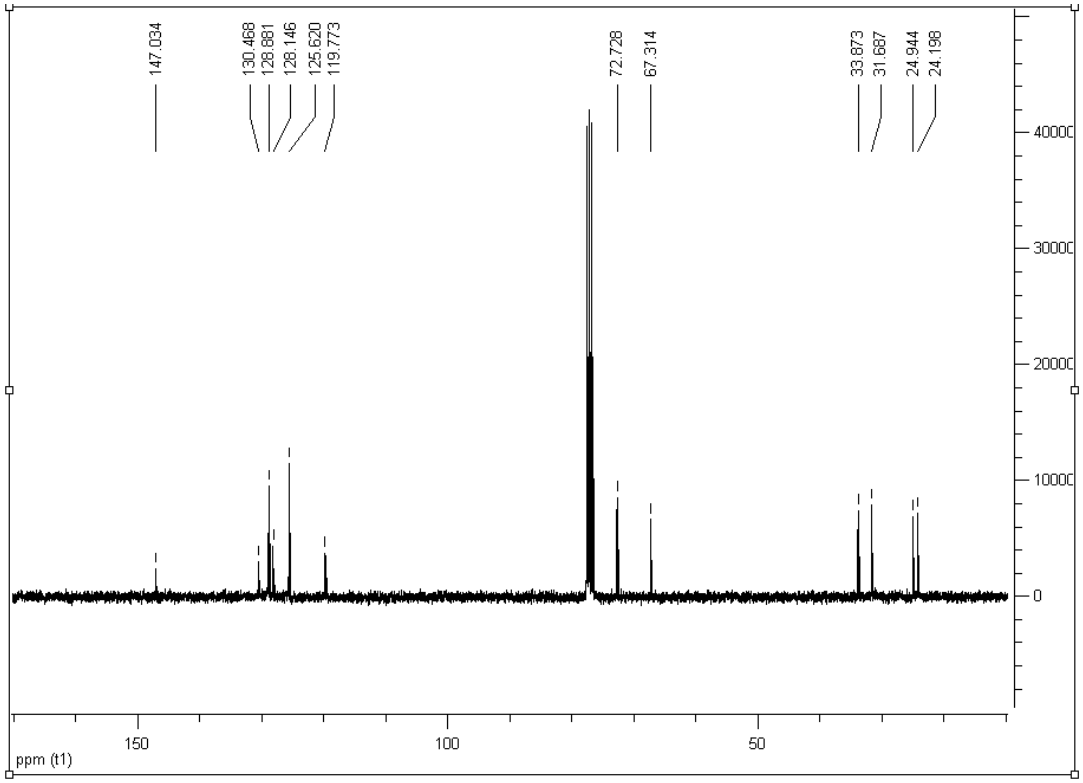
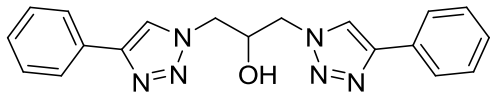
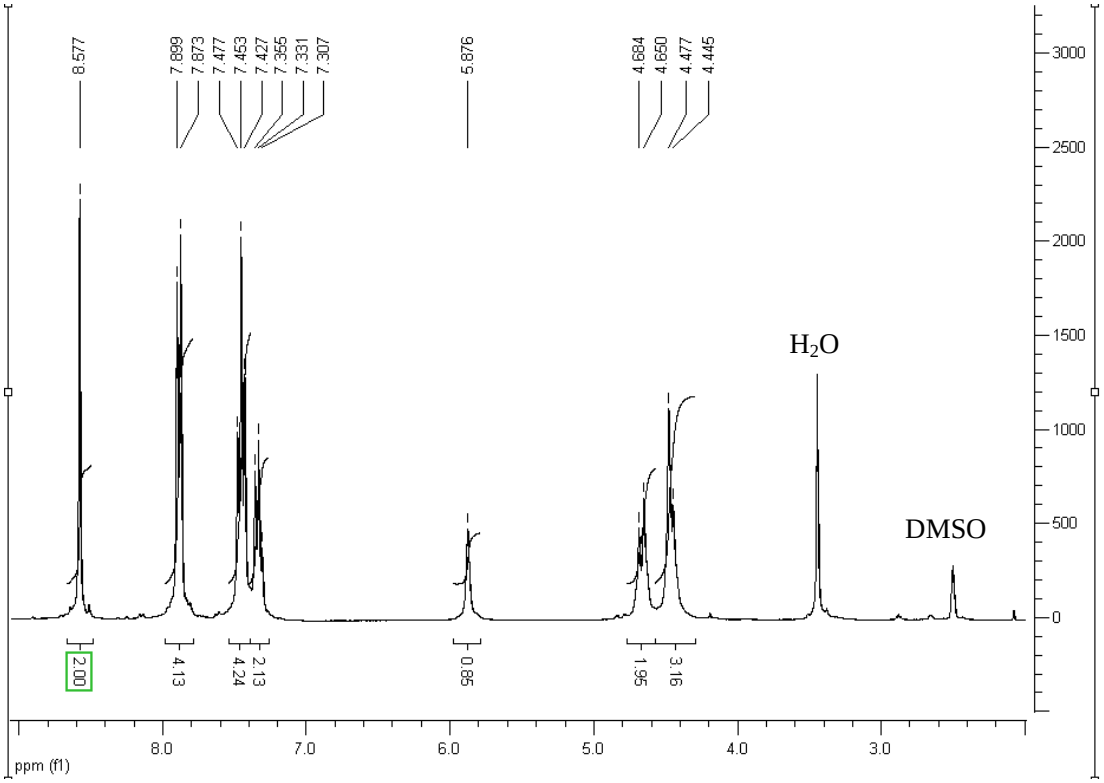


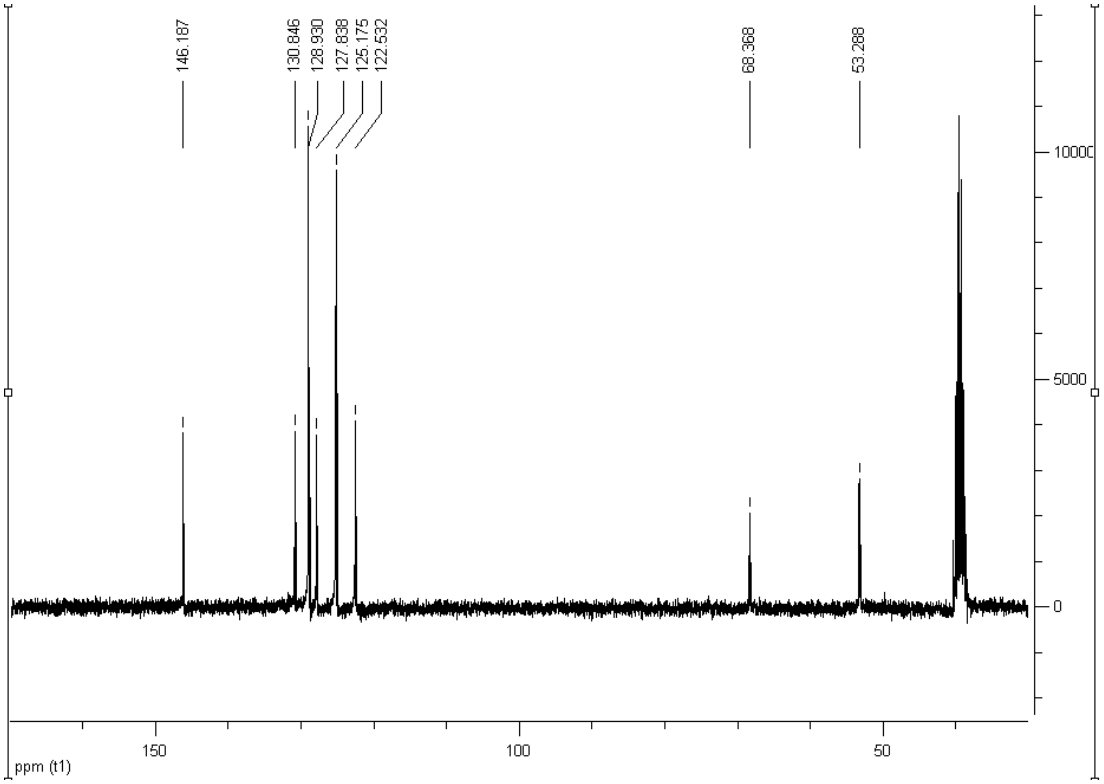


The above spectra is ^{1}H NMR, and the below spectra is ^{13}C NMR

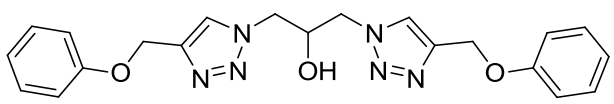


19

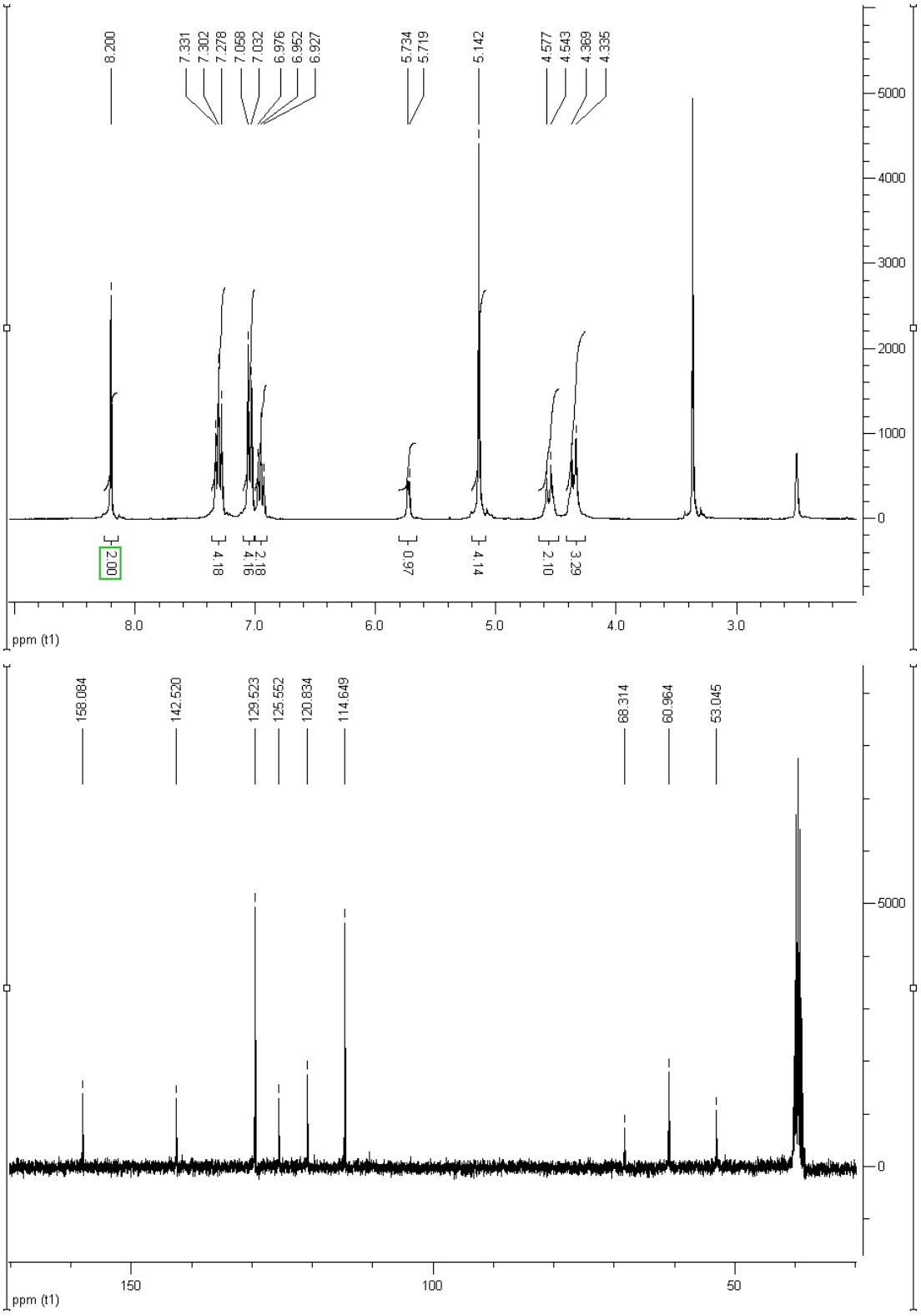




The above spectra is ^{1}H NMR, and the below spectra is ^{13}C NMR

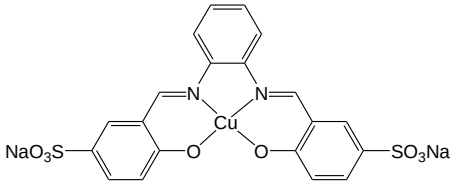


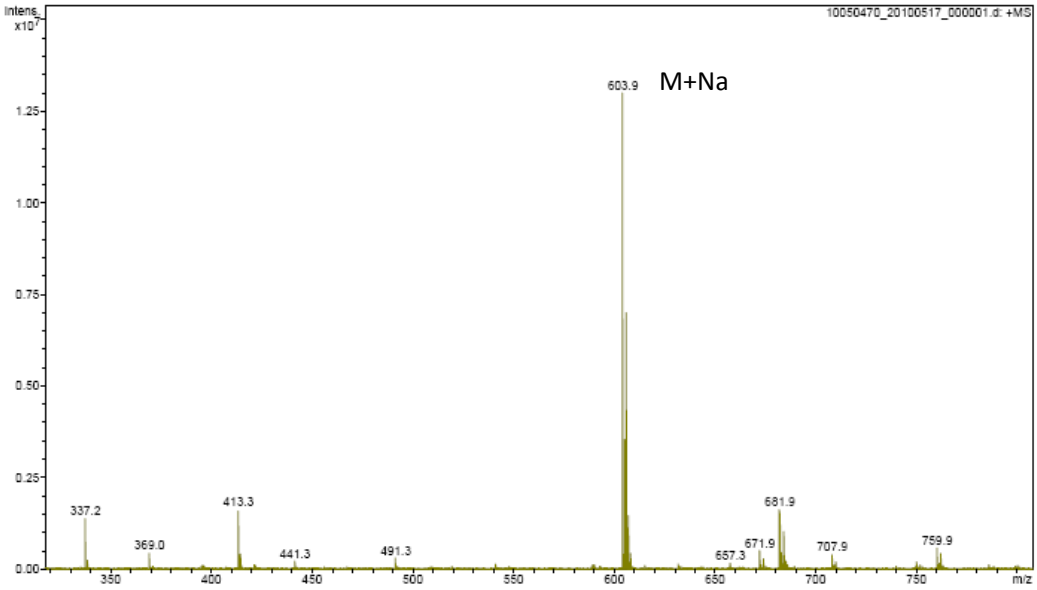
20

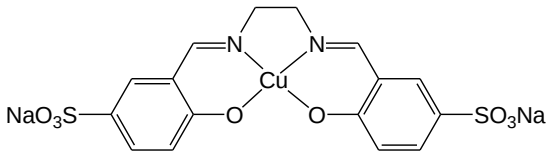


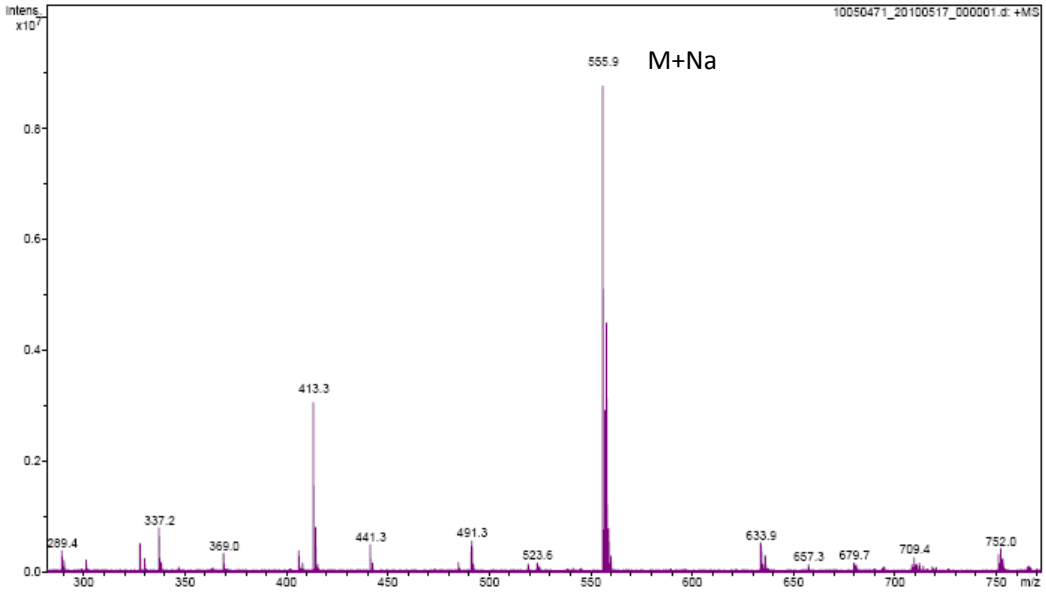
The above spectra is ^{1}H NMR, and the below spectra is ^{13}C NMR

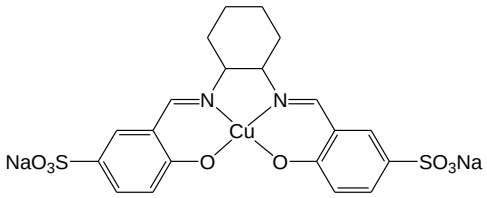
7. ESI-MS spectra of catalysts and products

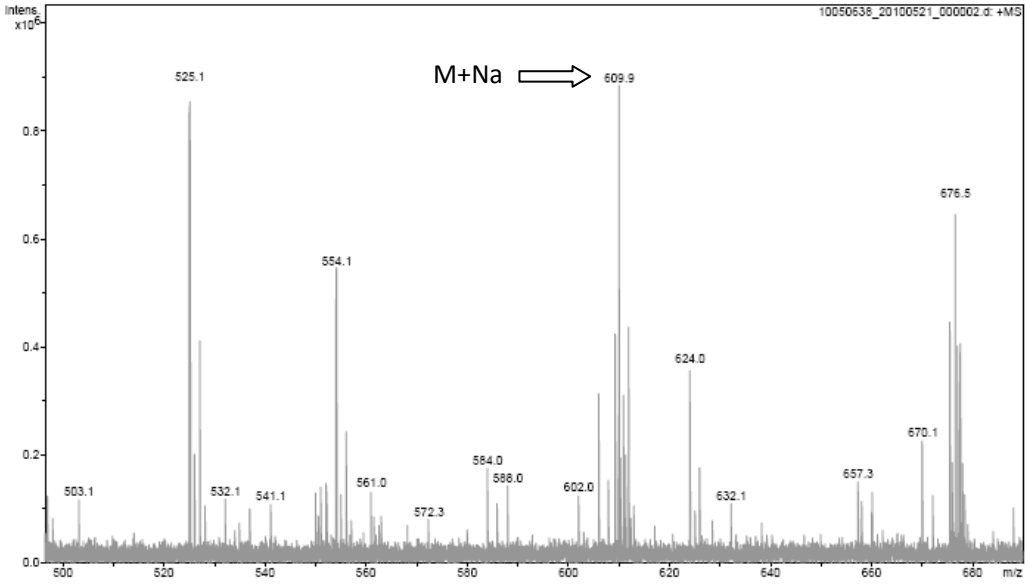


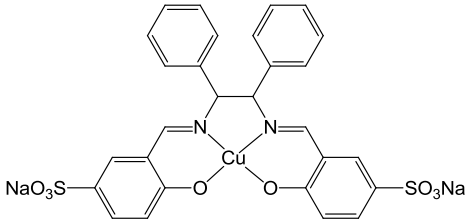


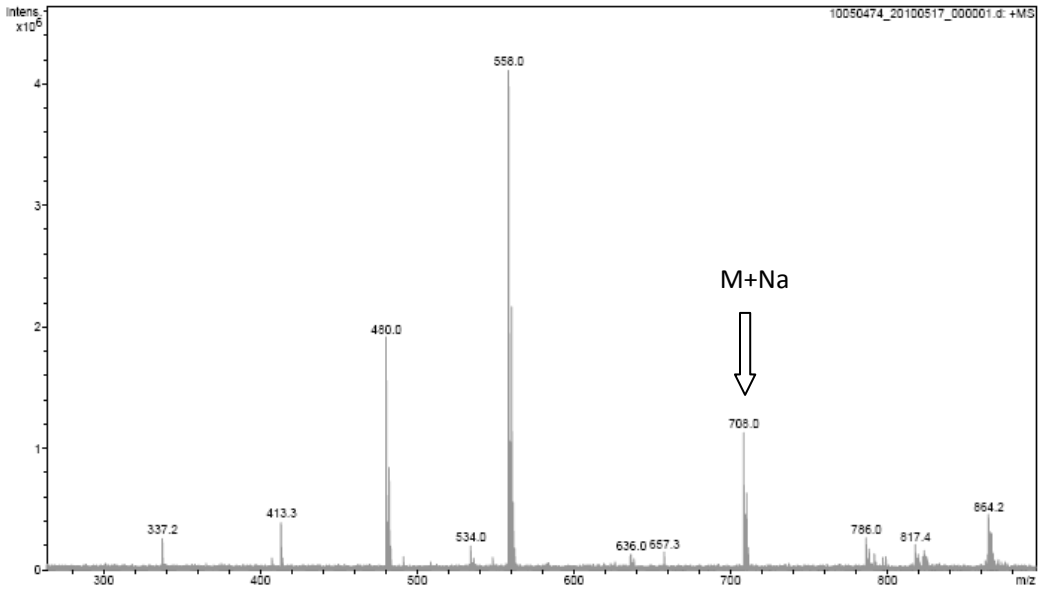


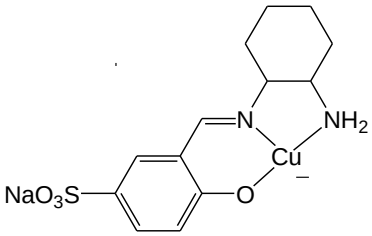



N
N
Cu
O
O
NaO3S
SO3Na

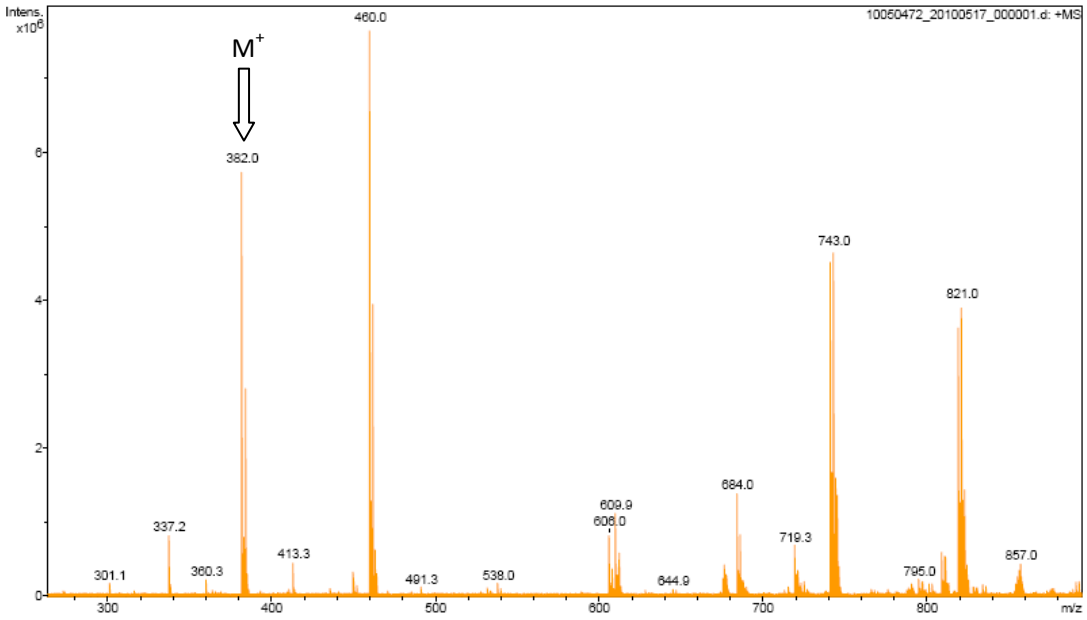

Intens.
x10^6
10050638_20100521_000002.d: +MS
M+Na
525.1
609.9
676.5
554.1
624.0
670.1
584.0
586.0
657.3
561.0
602.0
503.1
532.1
541.1
572.3
632.1
0.0
0.2
0.4
0.6
0.8
500
520
540
560
580
600
620
640
660
680
m/z

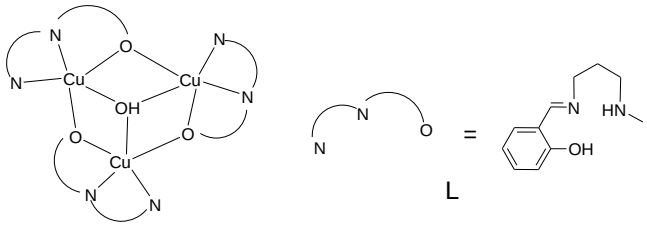

N
N
Cu
O
O
NaO3S
SO3Na


Intens.
x10^6
10050474_20100517_000001.d: +MS
558.0
480.0
M+Na
708.0
337.2
413.3
534.0
636.0
657.3
786.0
817.4
864.2
m/z



Cu-5



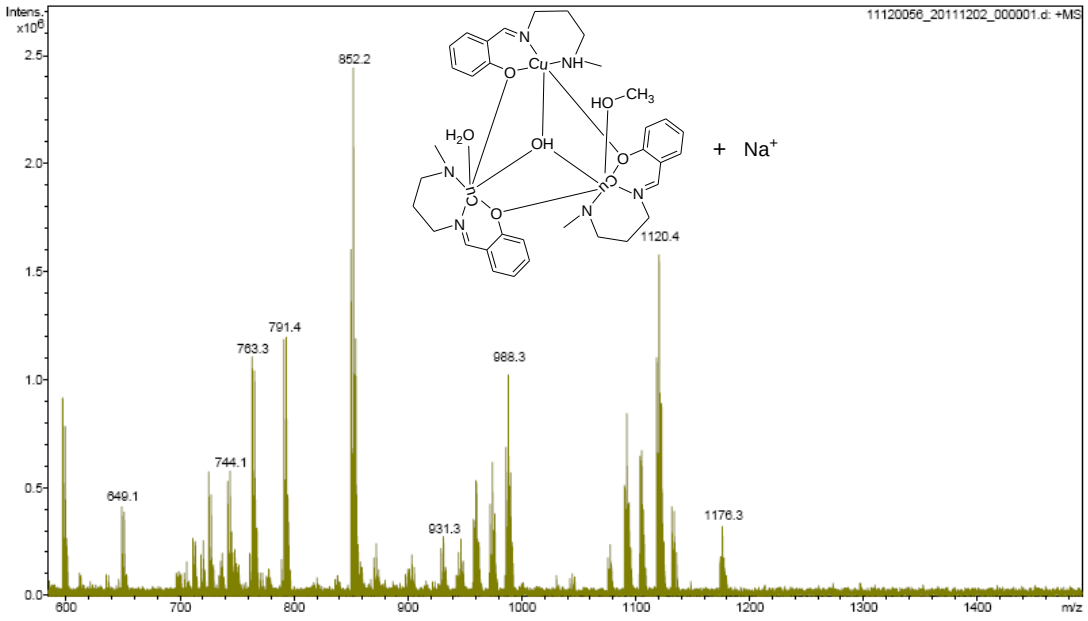


Cu-7

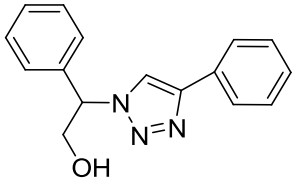
Peking University Mass Spectrometry Analysis Report

Analysis Info

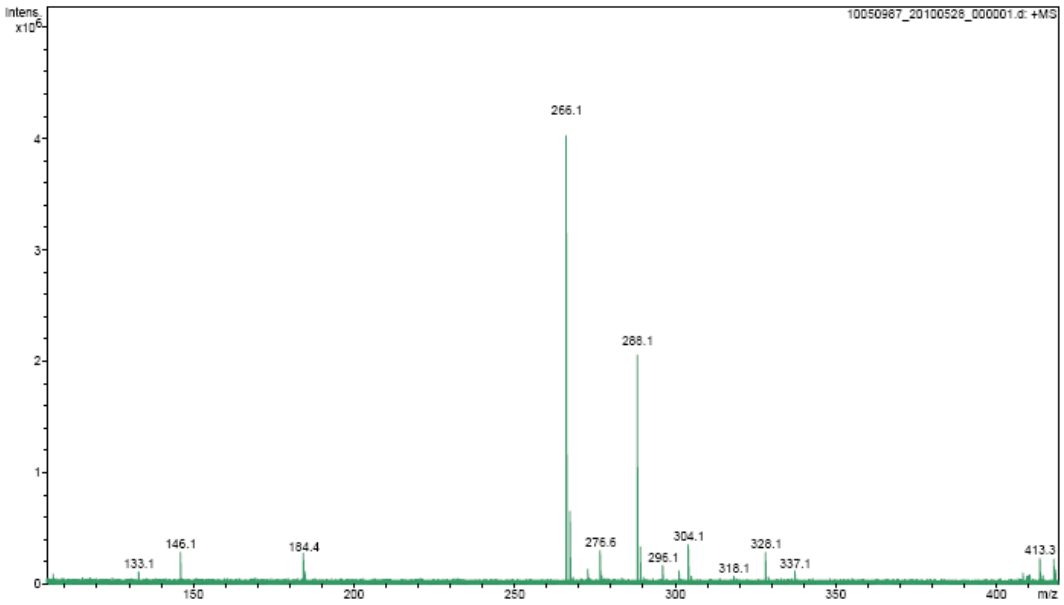
Analysis Name	11120056_20111202_000001.d	Acquisition Date	12/2/2011 4:36:04 PM
Sample	PhNCu3	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University

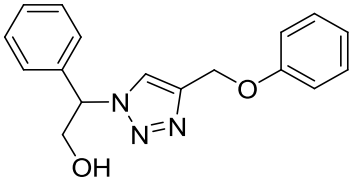


Bruker Compass DataAnalysis 4.0 printed: 12/2/2011 4:38:32 PM Page 1 of 1

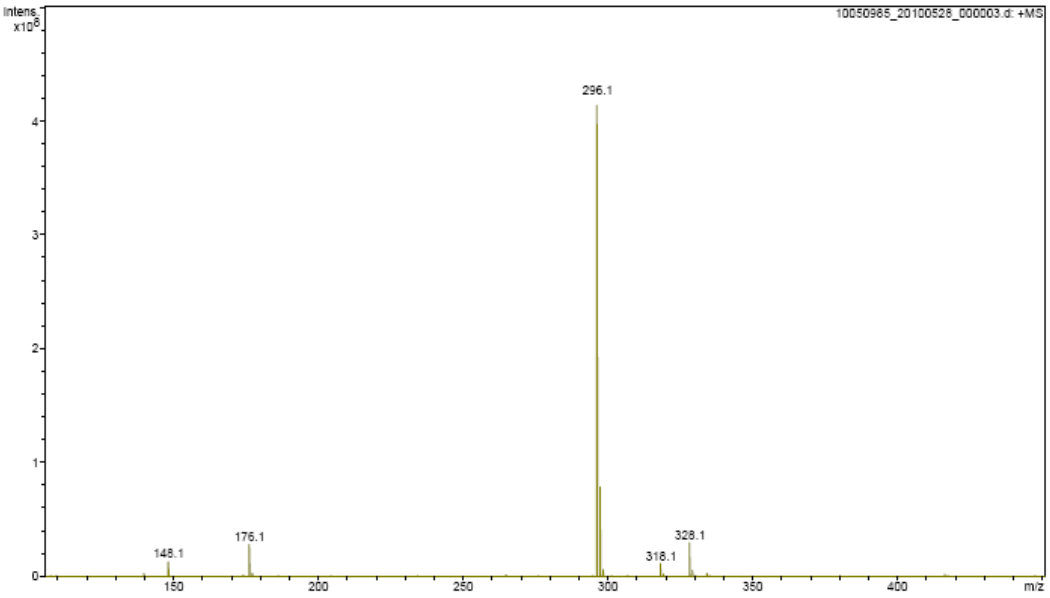


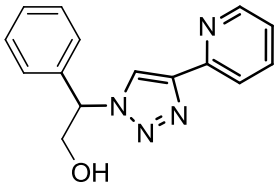
9



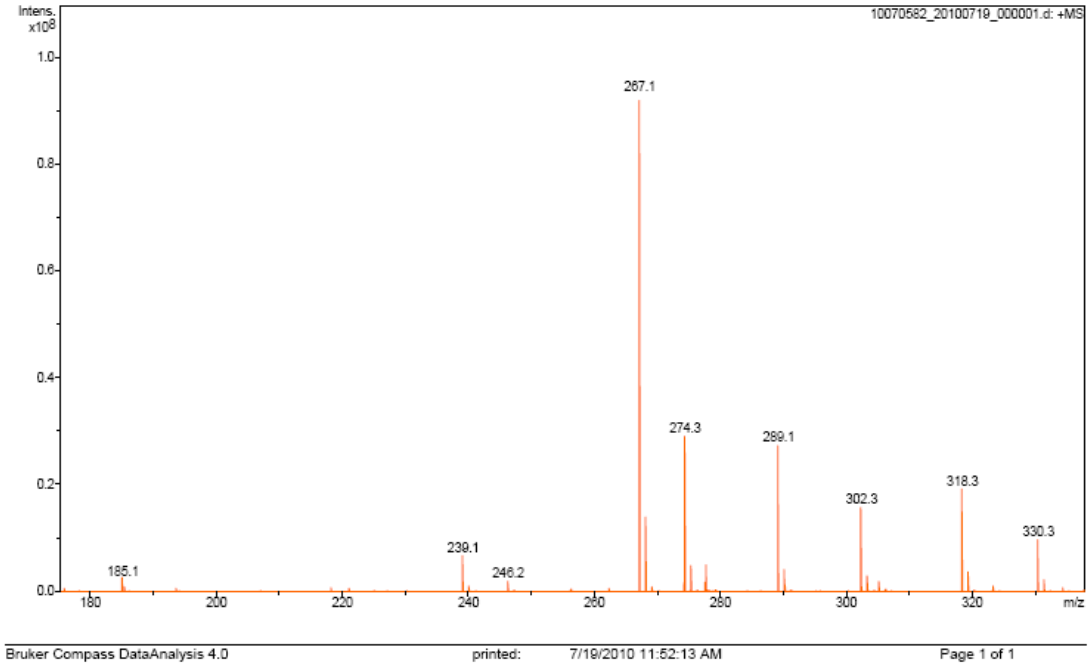

N
N=N
O
OH

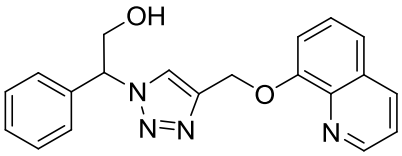
10


Intens.
x10^6
10050985_20100528_000003.d: +MS
296.1
176.1
148.1
328.1
318.1
m/z


N
N
N
N
OH

11


Intens.
x10^8
1.0
0.8
0.6
0.4
0.2
0.0
10070582_20100719_000001.d: +MS
267.1
274.3
289.1
302.3
318.3
330.3
239.1
246.2
185.1
180
200
220
240
260
280
300
320
m/z
Bruker Compass DataAnalysis 4.0
printed:
7/19/2010 11:52:13 AM
Page 1 of 1

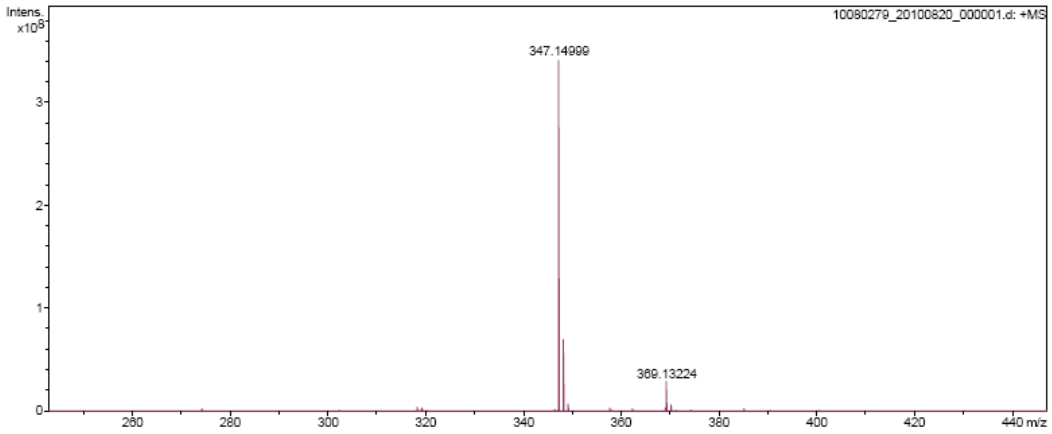


12

Peking University Mass Spectrometry Sample Analysis Report

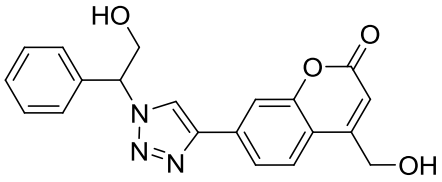
Analysis Info

Analysis Name	10080279_20100820_000001.d	Acquisition Date	8/20/2010 5:03:31 PM
Sample	Quin-styrene	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
347.14999	1	C 20 H 19 N 4 O 2	100.00	347.15025	0.3	0.8	15.1	13.5	even	ok
369.13224	1	C 20 H 18 N 4 Na O 2	100.00	369.13220	-0.0	-0.1	13.6	13.5	even	ok

Bruker Compass DataAnalysis 4.0 printed: 12/1/2011 5:20:26 PM Page 1 of 1

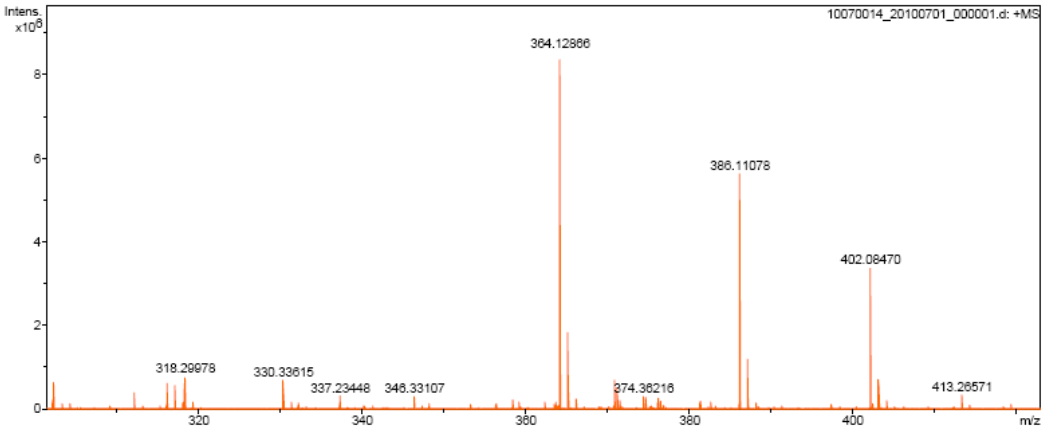


13

Peking University Mass Spectrometry Sample Analysis Report

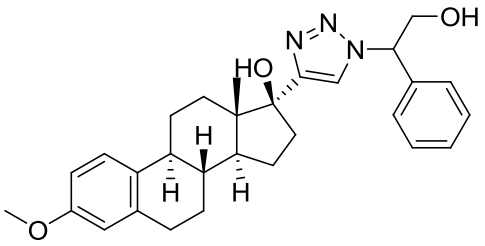
Analysis Info

Analysis Name	10070014_20100701_000001.d	Acquisition Date	7/1/2010 2:26:08 PM
Sample	Click 8	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
364.12866	1	C 20 H 18 N 3 O 4	100.00	364.12918	0.5	1.4	7.6	13.5	even	ok
386.11078	1	C 20 H 17 N 3 Na O 4	100.00	386.11113	0.4	0.9	8.0	13.5	even	ok
402.08470	1	C 20 H 17 K N 3 O 4	100.00	402.08506	0.4	0.9	24.1	13.5	even	ok

Bruker Compass DataAnalysis 4.0 printed: 12/1/2011 5:16:58 PM Page 1 of 1

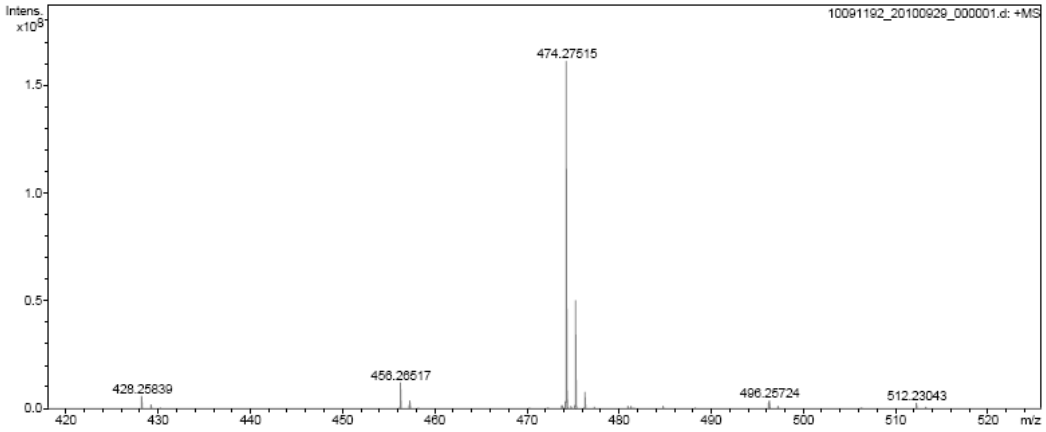


14

Peking University Mass Spectrometry Sample Analysis Report

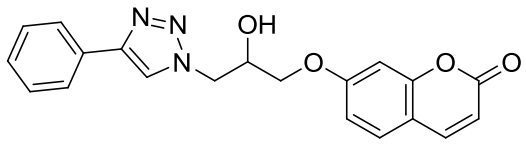
Analysis Info

Analysis Name	10091192_20100929_000001.d	Acquisition Date	9/29/2010 10:35:35 AM
Sample	Click-Mes-white	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
474.27515	1	C 29 H 36 N 3 O 3	100.00	474.27512	-0.0	-0.1	10.2	13.5	even	ok

Bruker Compass DataAnalysis 4.0 printed: 12/1/2011 5:25:23 PM Page 1 of 1

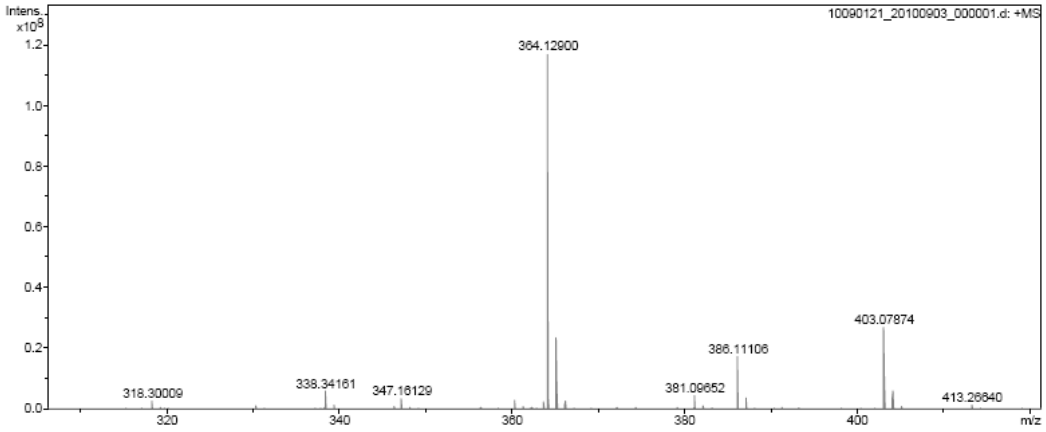


15

Peking University Mass Spectrometry Sample Analysis Report

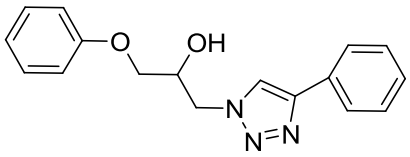
Analysis Info

Analysis Name	10090121_20100903_000001.d	Acquisition Date	9/3/2010 2:21:08 PM
Sample	Click-coumarin epoxide	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University

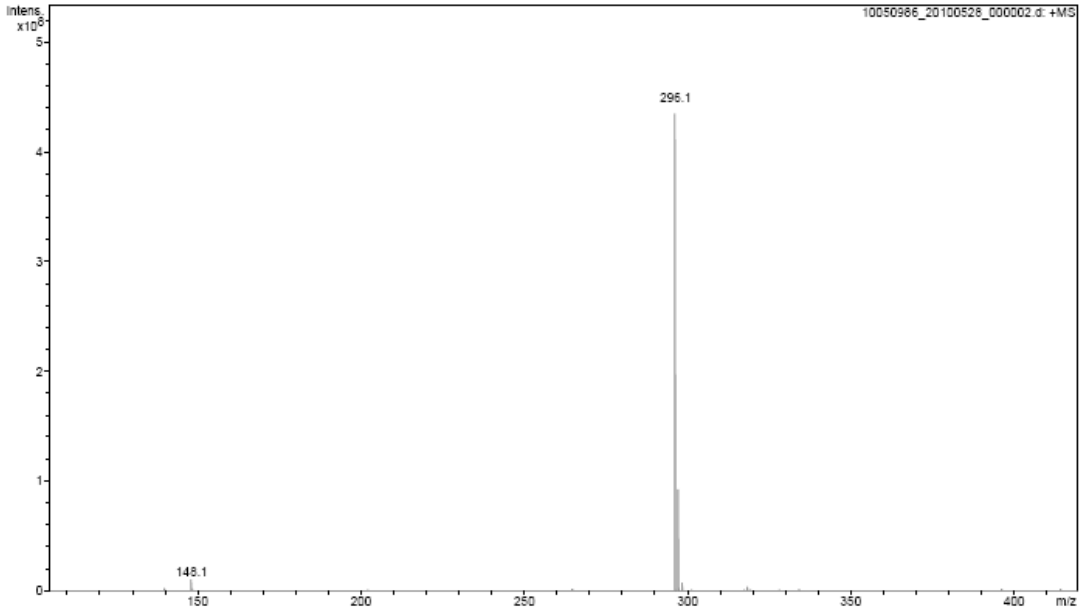


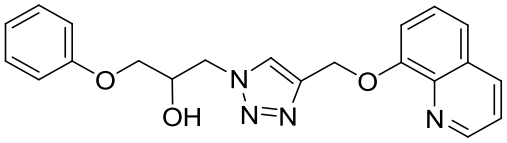
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
364.12900	1	C 20 H 18 N 3 O 4	100.00	364.12918	0.2	0.5	16.6	13.5	even	ok

Bruker Compass DataAnalysis 4.0 printed: 12/1/2011 5:23:20 PM Page 1 of 1


O
OH
N
N
N

16


Intens.
x10^6
5
4
3
2
1
0
10050986_20100528_000002.d: +MS
296.1
148.1
150
200
250
300
350
400
m/z

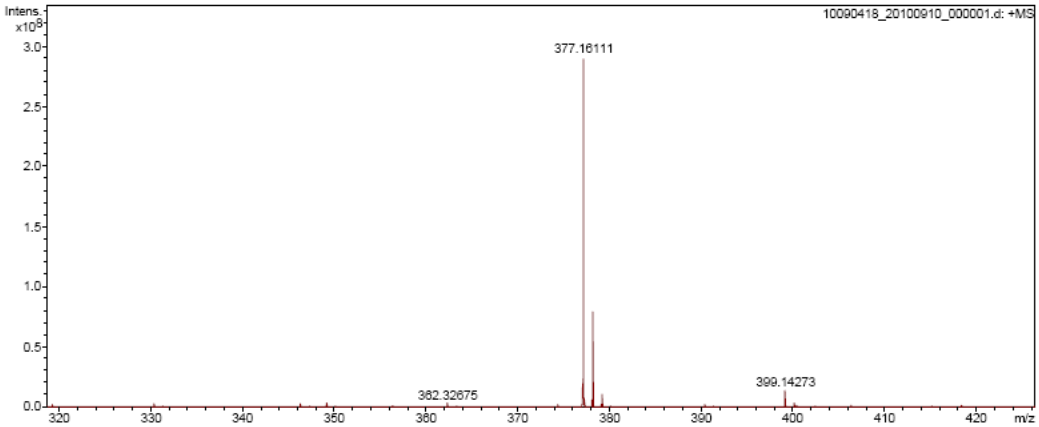


17

Peking University Mass Spectrometry Sample Analysis Report

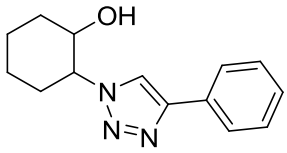
Analysis Info

Analysis Name	10090418_20100910_000001.d	Acquisition Date	9/10/2010 2:51:12 PM
Sample	Click-QuinPro	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University

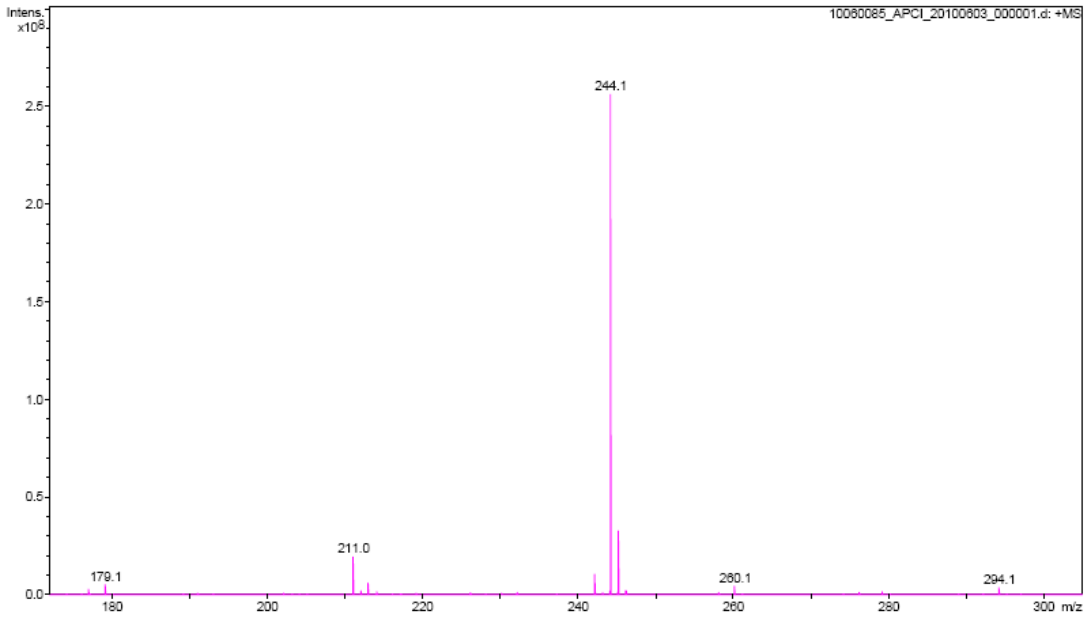


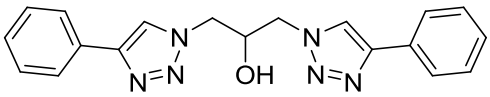
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
377.16111	1	C 21 H 21 N 4 O 3	100.00	377.16082	-0.3	-0.8	19.9	13.5	even	ok
399.14273	1	C 21 H 20 N 4 Na O 3	100.00	399.14276	0.0	0.1	8.4	13.5	even	ok

Bruker Compass DataAnalysis 4.0 printed: 12/1/2011 5:24:22 PM Page 1 of 1

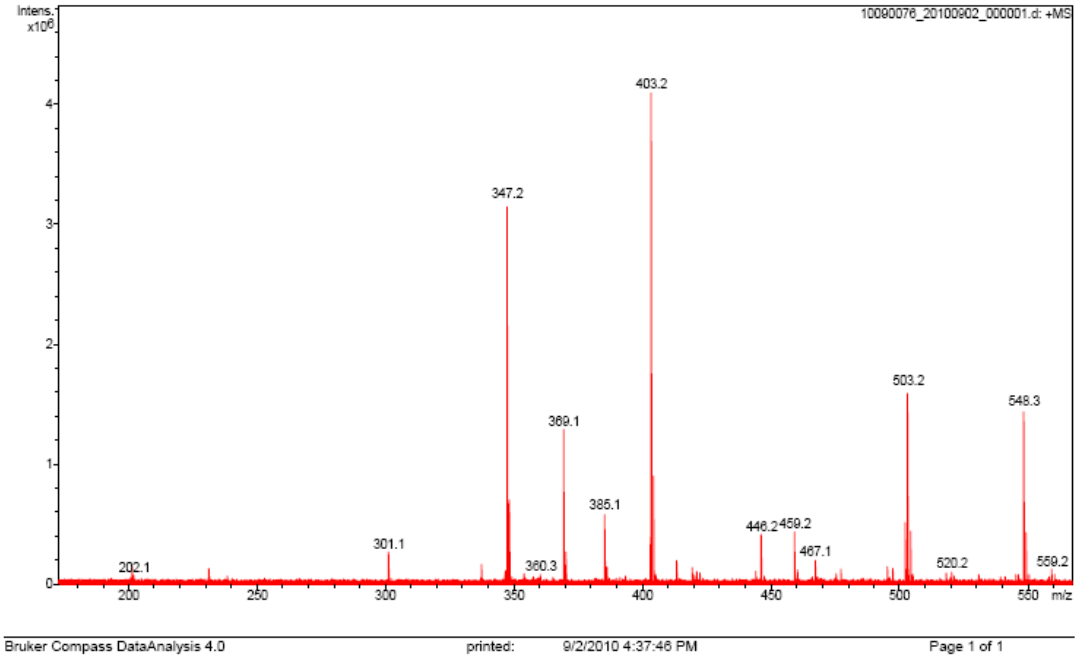

OH
N
N
N

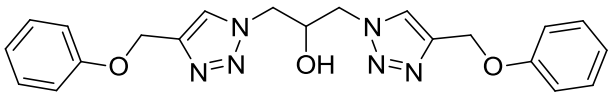
18


Intens.
x10^8
10060085_APCI_20100603_000001.d: +MS
244.1
211.0
179.1
260.1
294.1
2.5
2.0
1.5
1.0
0.5
0.0
180
200
220
240
260
280
300 m/z


N
N=N
OH
N
N=N

19


Intens.
x10^6
10090076_20100902_000001.d: +MS
403.2
347.2
503.2
548.3
369.1
385.1
446.2
459.2
301.1
467.1
202.1
360.3
520.2
559.2
200
250
300
350
400
450
500
550
m/z
Bruker Compass DataAnalysis 4.0
printed:
9/2/2010 4:37:46 PM
Page 1 of 1

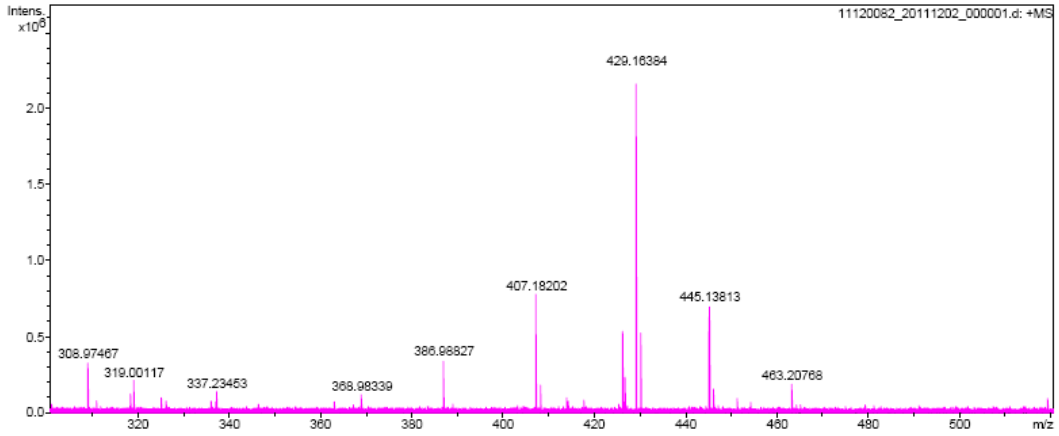


20

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	11120082_20111202_000001.d	Acquisition Date	12/2/2011 5:09:21 PM
Sample	Triazole-2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
407.18202	1	C 21 H 23 N 6 O 3	100.00	407.18262	0.6	1.5	21.1	13.5	even	ok
429.16384	1	C 21 H 22 N 6 Na O 3	100.00	429.16456	0.7	1.7	21.4	13.5	even	ok

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