Supporting information

Synthesis ,insecticidal and fungicidal activities of methyl 2-(methoxyimino)-2-(2-((1-(N- nitrocarbamimidoyl)-2-hydrocarbylidenehydrazinyl)-methyl)phenyl)acetates

Xiaoyong Yuan,[ς,a,b] Changqing Jia,[ς,a] Yongqiang Ma,[a] Dongyan Yang,[a] Changhui Rui,[c] Zhaohai Qin[a]*

a. College of Science, China Agricultural University, Beijing 100193，China

b. National Navel Orange Engineering Research Center, Gannan Normal University, Ganzhou 341000, Jiangxi Province, China

c. Institute of Plant Protection, Chinese Academy of Agricultural Sciences, Beijing 100193, China

[ς] these authors contributed the same to the article

Table of Contents

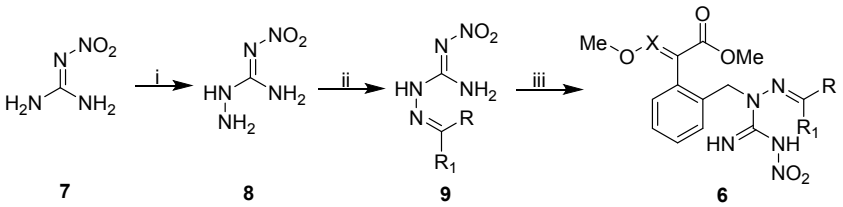
General synthesis procedure for Intermediate 8..... S2

General synthesis procedure for Intermediate 9..... S2

Spectrum date of compound 6..... .... S5

[1] H NMR date of (E)-methyl 2-(2-(bromomethyl)phenyl)-2-(methoxyimino)acetate.....S28

Scheme 1. Prepararion of title compounds



i. 85% hydrazine hydrate, 55°C, 70%; ii. RR_1CO, HOAc, MeOH, 3-5h; iii. (*E*)-methyl 2-(2-(bromomethyl)phenyl)-2-(methoxyimino) acetate, Cs_2CO_3, KI, DMF, 80°C

Synthesis procedure for Nitroaminoguanidine (8)

In a 1000 mL flask, a mixture of the nitroguanidine(**7**, 0.192 mol), water (250ml) was heated to 55 ℃ under stirring, 85% hydrazine hydrate (0.216 mol) was added dropwise to the mixture, the reaction was allowed to stir 15 minutes at 55℃. At this point, the solid was all dissolved in the water, then the solution was quickly cooled to about 20℃, the balanced concentrated hydrochloric acid was added to the solution until PH=5~6. The crude product was precipitated from the solution. The precipitate was filtrated and washed with water, and the crude product was recrystallized from hot water to afford the compound **8**.

Nitroaminoguanidine (**8**), white crystal, mp 134 - 136℃, yield 70%. ^{1}H NMR(DMSO-d_6)δ: 9.33(s,1H), 8.27(s,1H), 7.56(s,1H), 4.69(s,2H).

General synthesis procedure for Intermediate (9-01~9-04，9-07~9-23)

Method A: In a 250 mL flask, nitroaminoguanidine (8) (2.0 g,17 mmol) and glacial acetic acid (0.2 mL) were dissolved in menthol (100 mL), the mixture was heated at 50 °C, aldehyde (20 mmol) was added dropwise to the mixture, and the reaction was refluxed for 4 h. After completion, the solvent was removed under reduced pressure, and the resulting crude material was recrystallized using ethanol and petroleum ether (v/v, 3:1).

General synthesis procedure for Intermediate (9-05, 9-06)

Method B: In a 250 mL flask, nitroaminoguanidine (**8**) (2.0 g,17 mmol) and concentrated hydrochloric acid (0.2 mL) were dissolved in menthol (100 mL), the mixture was heated at 50 °C, ketone(20 mmol) was added dropwise to the mixture, and the mixture was refluxed for 6 h. After completion, the solvent was removed under reduced pressure, and the resulting crude material was recrystallized using methanol.

2-Butylidene-N-nitrohydrazinecarboximidamide(9-01): yellow solid, mp 100 - 102℃, yield 80%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.91 (t, 3H), 1.48 - 1.55 (m, 2H), 2.23 - 2.27 (m, 2H), 7.53 (t, 1H), 8.02 (brs, 1H), 8.64 (brs, 1H), 11.46 (brs, 1H).

2-(2-Methylpentylidene)-N-nitrohydrazinecarboximidamide(9-02): yellowish solid, mp 102 - 104℃, yield 82%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.88 (t, J = 6.90, 3H), 1.04 (d, J = 6.81, 3H), 1.24 - 1.48 (m, 4H), 2.38 - 2.51 (m, 1H), 7.43 (d, J = 5.97, 1H), 7.97 (brs, 1H), 8.65 (brs, 1H), 11.43 (s, 1H).

2-(2-Ethylbutylidene)-N-nitrohydrazinecarboximidamide(9-03): white solid, mp 134 - 136℃, yield 75%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.91 (t, 6H), 1.45 - 1.60 (m, 4H), 2.10 - 2.17 (m, 1H), 7.02 (brs, 1H), 7.55 (d, 1H), 8.76 (brs, 1H), 10.98 (brs, 1H).

2-Heptylidene-N-nitrohydrazinecarboximidamide(9-04): yellow solid, mp 93 - 95℃, yield 70%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.91(t, J = 1.62, 3H), 1.25 - 1.38 (m, 6H), 1.50 - 1.59 (m, 2H), 2.29 - 2.36 (m, 2H), 6.98 (brs, 1H), 7.70 (t, J = 5.46, 1H), 8.67 (brs, 1H), 10.81 (brs, 1H).

N-Nitro-2-(propan-2-ylidene)hydrazinecarboximidamide(9-05): white solid, mp 164 - 166℃,

yield 80%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.92 (s, 3H), 1.99 (s, 3H), 7.99 (brs, 1H), 8.64 (brs, 1H), 10.76 (s, 1H).

N-Nitro-2-(pentan-3-ylidene)hydrazinecarboximidamide(9-06): white solid, mp 134 - 136℃, yield 75%. ^{1}H NMR (300 MHz, DMSO-d_6) 0.91(t,6H) ,1.45-1.60(m,4H), 2.10 -2.17 (m,1H), 7.02(brs,1H), 7.55(d,1H), 8.76 (brs,1H), 10.98(brs,1H)

2-(Furan-2-ylmethylene)-N-nitrohydrazinecarboximidamide(9-07): yellowish solid, mp 222 - 224℃, yield 87%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.67 - 7.88 (m, 3H), 8.08 (s, 1H), 8.18 (brs, 1H), 8.80 (brs, 1H), 11.83 (s, 1H).

2-Benzylidene-N-nitrohydrazinecarboximidamide(9-08): white solid, mp 195 - 197℃, yield 86%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.42 - 7.91 (m, 5H), 8.17 (s, 1H), 8.55 (brs, 1H), 8.84 (brs, 1H), 11.82 (s, 1H).

2-(4-Cyanobenzylidene)-N-nitrohydrazinecarboximidamide(9-09): yellowish solid, mp 244 - 246℃, yield 85%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.89 - 8.12 (m, 4H), 8.19 (s, 1H), 8.78 (brs, 1H), 8.93 (brs, 1H), 12.00 (s, 1H).

2-(4-Chlorobenzylidene)-N-nitrohydrazinecarboximidamide(9-10): white solid, mp 186 - 188℃, yield 92%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.48 - 7.95 (m, 4H), 8.15 (s, 1H), 8.64 (brs, 1H, 8.87 (brs, 1H), 11.87 (s, 1H).

2-(2-Chlorobenzylidene)-N-nitrohydrazinecarboximidamide(9-11): white solid, mp 207 - 209℃, yield 90%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.38 - 8.42 (m, 4H), 8.57 (s, 1H), 8.69 (brs, 1H), 8.91 (brs, 1H), 11.97 (s, 1H).

2-(2,4-Dichlorobenzylidene)-N-nitrohydrazinecarboximidamide(9-12): yellowish solid, mp 228 - 230℃, yield 92%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.48 - 8.46 (m, 4H), 8.51 (s, 1H), 8.76 (brs, 1H), 8.94 (brs, 1H), 12.00 (s, 1H).

N-Nitro-2-(4-nitrobenzylidene)hydrazinecarboximidamide(9-13): yellow solid, mp 264 - 266℃, yield 95%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.15 - 8.29 (m, 5H), 8.82 (brs, 1H), 8.95 (brs, 1H), 12.05 (s, 1H).

N-Nitro-2-(3-nitrobenzylidene)hydrazinecarboximidamide(9-14): yellow solid, mp 256 - 258℃, yield 91%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.69 - 8.32 (m, 4H), 8.76 (s, 1H), 8.89 (brs, 2H), 11.98 (s, 1H).

2-(4-(*tert*-Butyl)benzylidene)-N-nitrohydrazinecarboximidamide(9-15): white solid, mp 193 - 195℃, yield 89%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.30 (s, 9H), 7.46 (d, J = 8.43, 2H), 7.79 (d, J = 8.46, 2H), 8.14 (s, 1H), 8.50 (brs, 1H), 8.83 (brs, 1H), 11.80 (s, 1H).

2-(4-Methylbenzylidene)-N-nitrohydrazinecarboximidamide(9-16): white solid, mp 201 - 203℃, yield 84%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 2.34 (s, 3H), 7.24 - 7.78 (m, 4H), 8.13 (s, 1H), 8.50 (brs, 1H), 8.80 (brs, 1H), 11.77 (s, 1H).

2-(4-Methoxybenzylidene)-N-nitrohydrazinecarboximidamide(9-17): white solid, mp 202 - 204℃, yield 92%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.81 (s, 3H), 6.97 - 7.85 (m, 4H), 8.11 (s, 1H), 8.47 (brs, 1H), 8.78 (brs, 1H), 11.73 (s, 1H).

2-(3-Methoxybenzylidene)-N-nitrohydrazinecarboximidamide(9-18): white solid, mp 212 - 214℃, yield 90%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.80 (s, 3H), 6.98 - 7.52 (m, 4H), 8.13 (s, 1H), 8.67 (brs, 1H), 8.84 (brs, 1H), 11.83 (s, 1H).

2-(2-Methoxybenzylidene)-N-nitrohydrazinecarboximidamide(9-19): white solid, mp 191 - 193℃, yield 88%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.85 (s, 3H), 6.98 - 8.20 (m, 4H), 8.52 (s, 1H), 8.52 (brs, 1H), 8.82 (brs, 1H), 11.77 (s, 1H).

2-(Benzo[d][1,3]dioxol-5-ylmethylene)-N-nitrohydrazinecarboximidamide(9-20): yellowish solid, mp 220 - 222℃, yield 88%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.09 (s, 2H), 6.95 - 7.75 (m, 3H), 8.07 (s, 1H), 8.56 (brs, 1H), 8.80 (brs, 1H), 11.72 (s,1H).

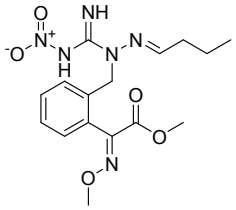
N-Nitro-2-(3-phenoxybenzylidene)hydrazinecarboximidamide(9-21): white solid, mp 211 - 213℃, yield 90%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.00 - 7.74 (m, 9H), 8.16 (s, 1H), 8.65 (brs, 1H), 8.84 (brs, 1H), 11.85 (s, 1H).

2-(3-Hydroxybenzylidene)-N-nitrohydrazinecarboximidamide(9-22): white solid, mp 210 - 212℃, yield 90%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.84 - 7.29 (m, 4H), 8.08 (s, 1H), 8.48 (brs, 1H, 8.81 (brs, 1H), 9.60 (s, 1H), 11.77 (s, 1H).

2-(2-Hydroxybenzylidene)-N-nitrohydrazinecarboximidamide(9-23): yellow solid, mp > 300℃, yield 89%. ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.82 – 8.04 (m, 4H),8.47 (s, 1H), 8.78 (brs, 2H), 10.02(s, 1H), 11.87 (s, 1H).

The NMR and HRMS spectrum of the title compounds (6-01~6-23):

6-01



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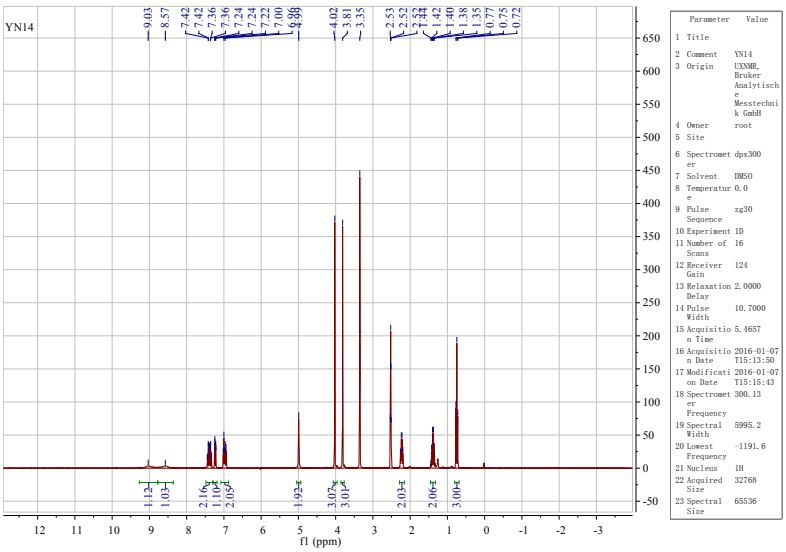

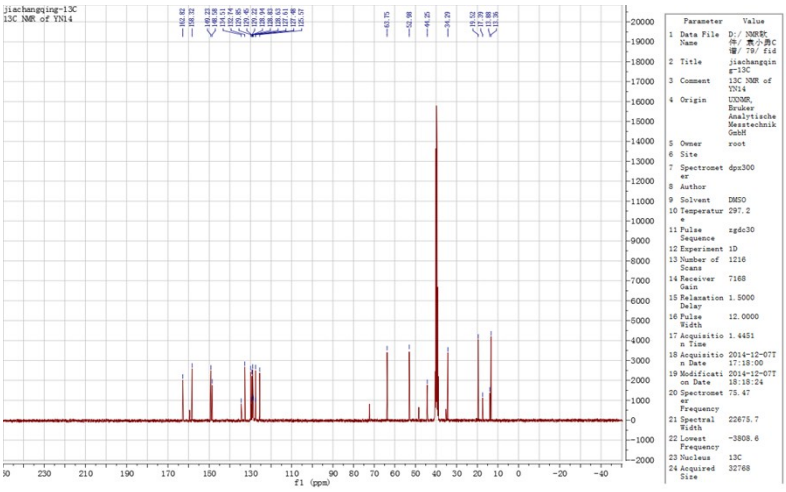

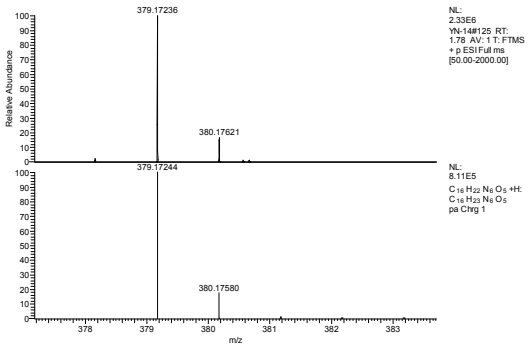

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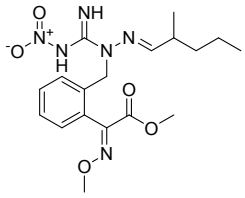

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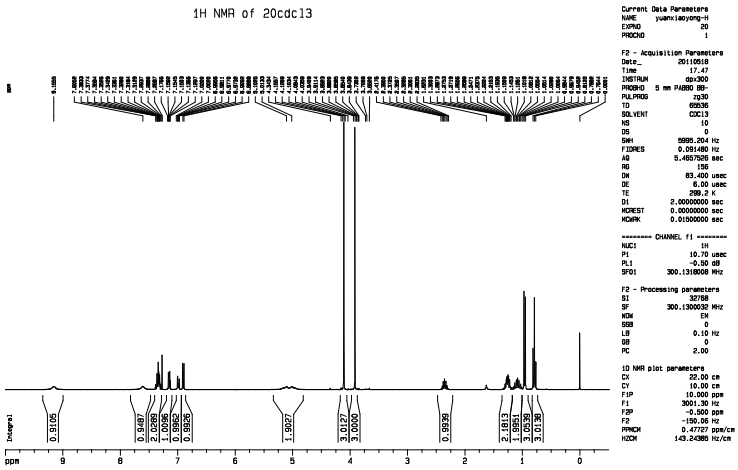

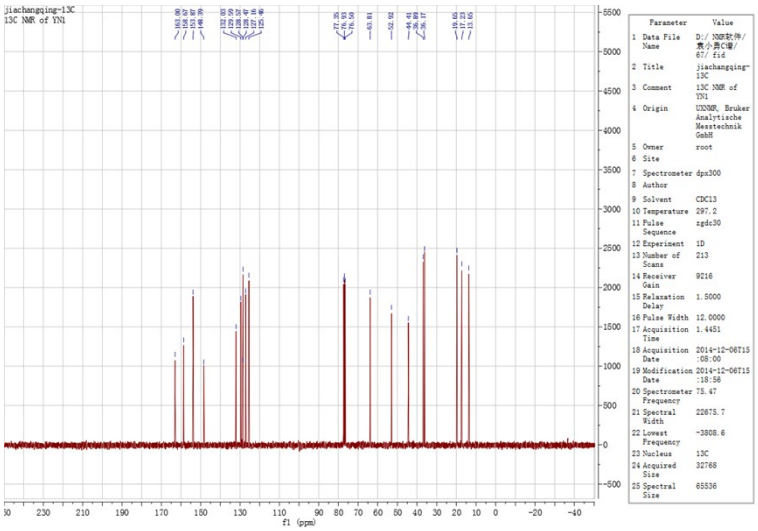

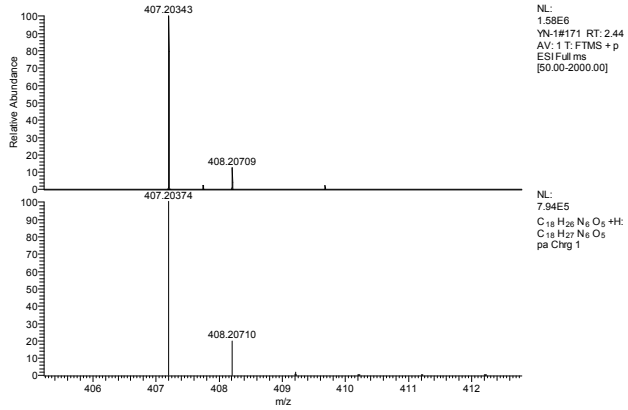

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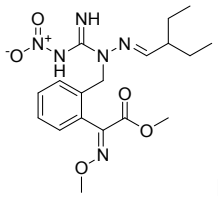

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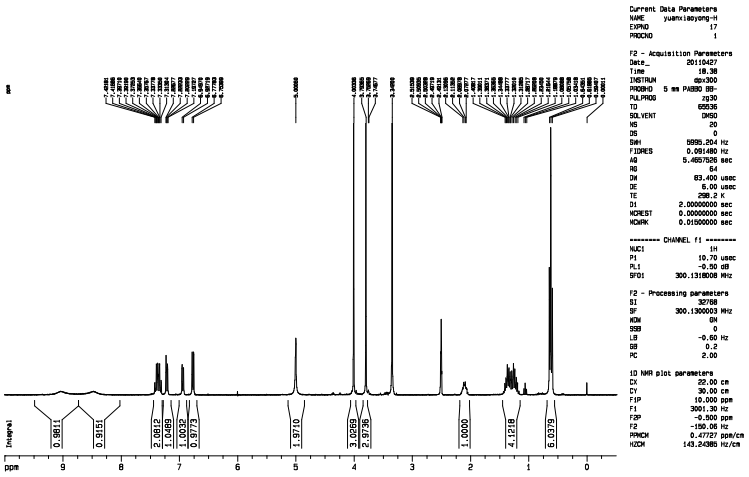

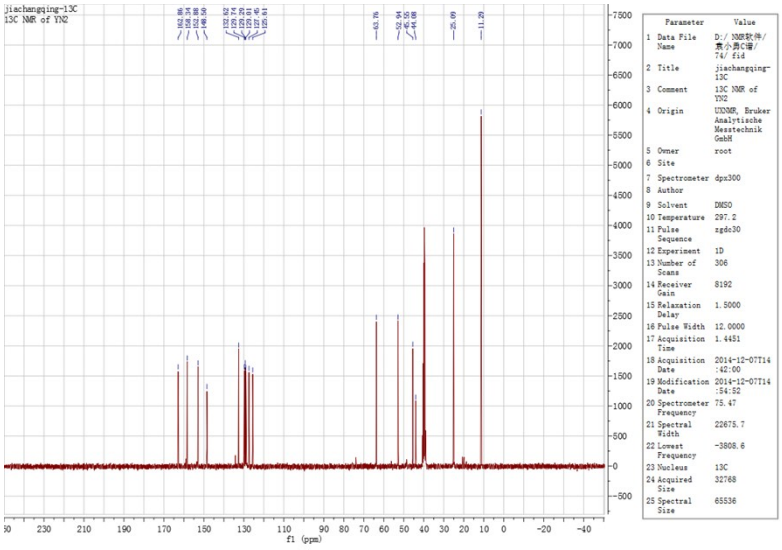

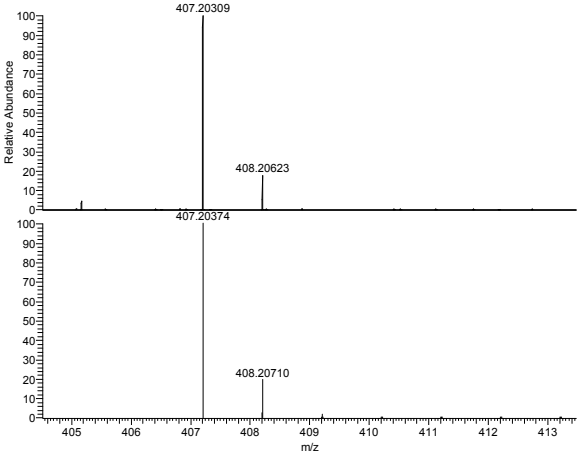

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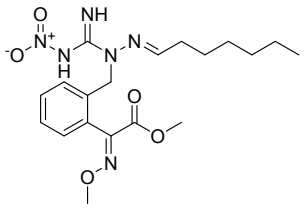

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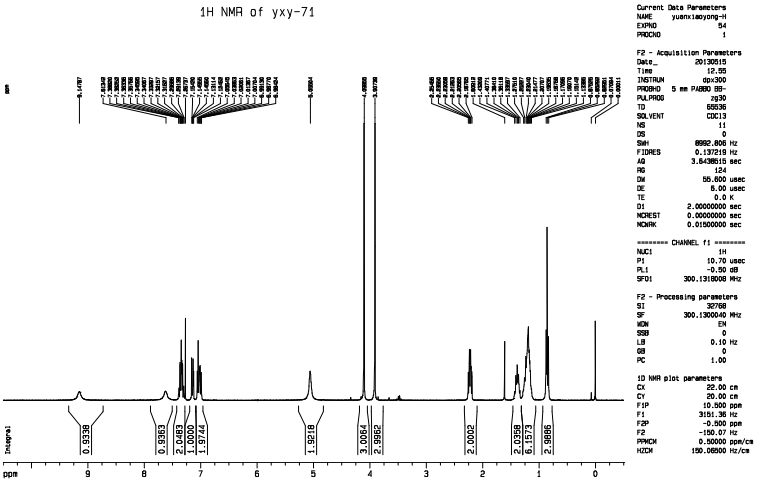

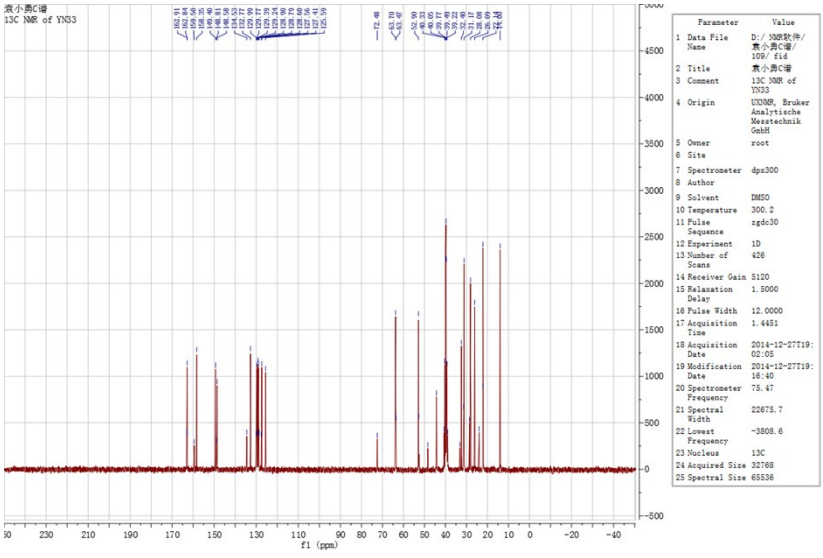

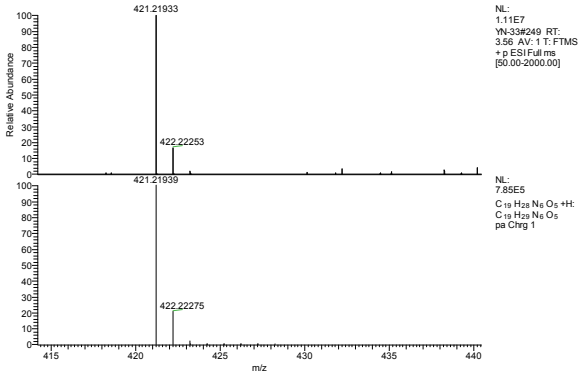

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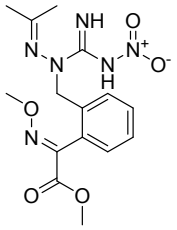

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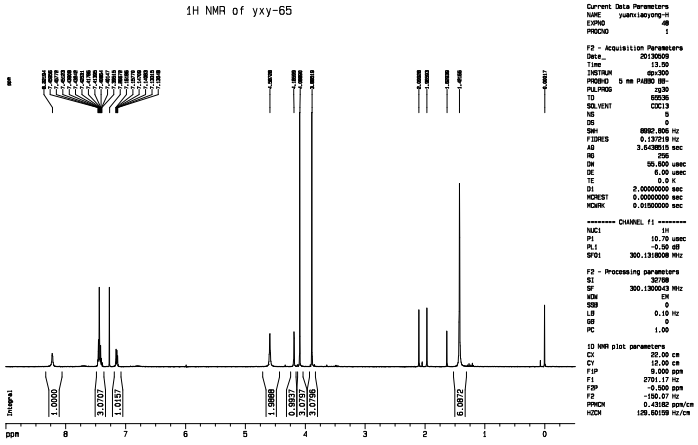

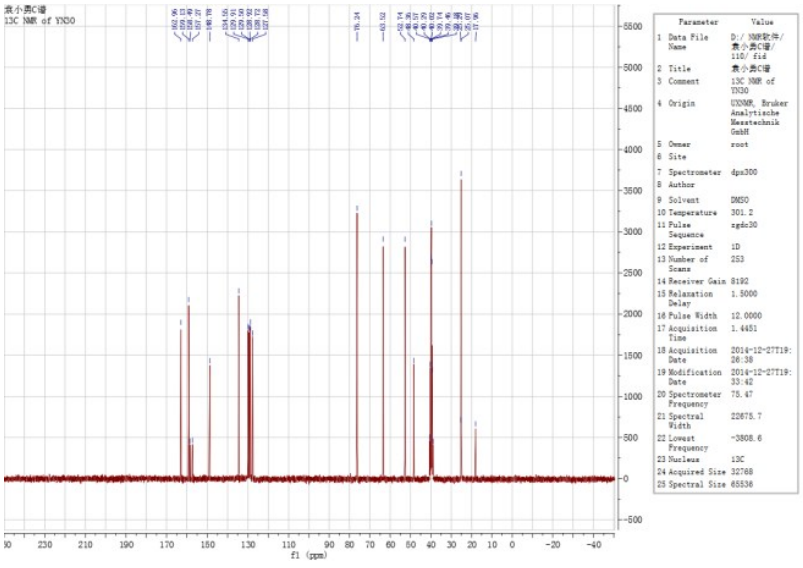

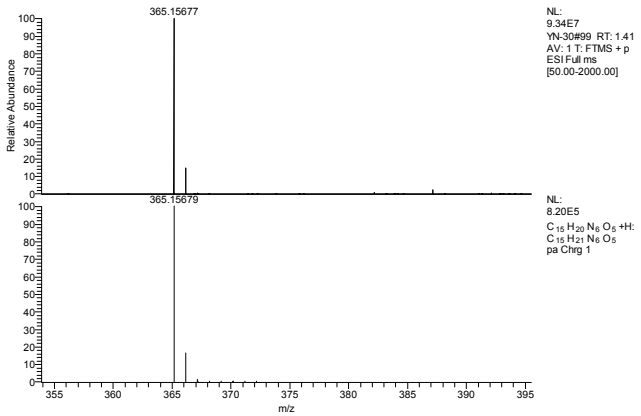

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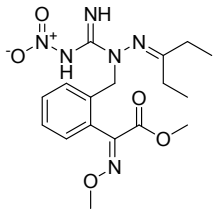

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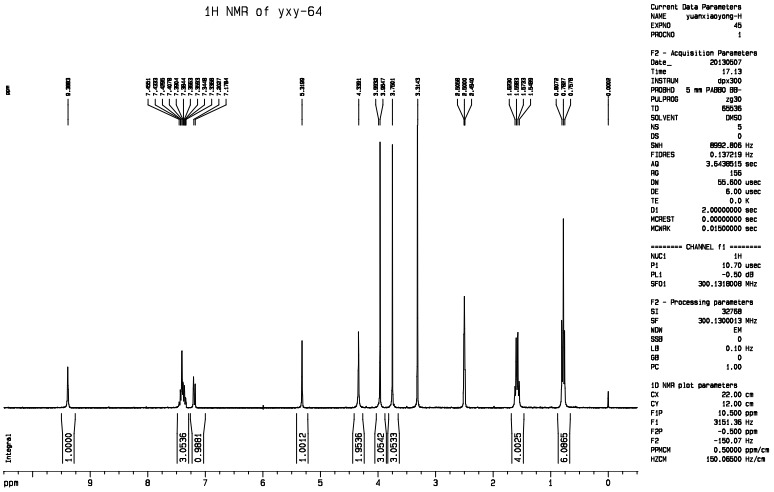

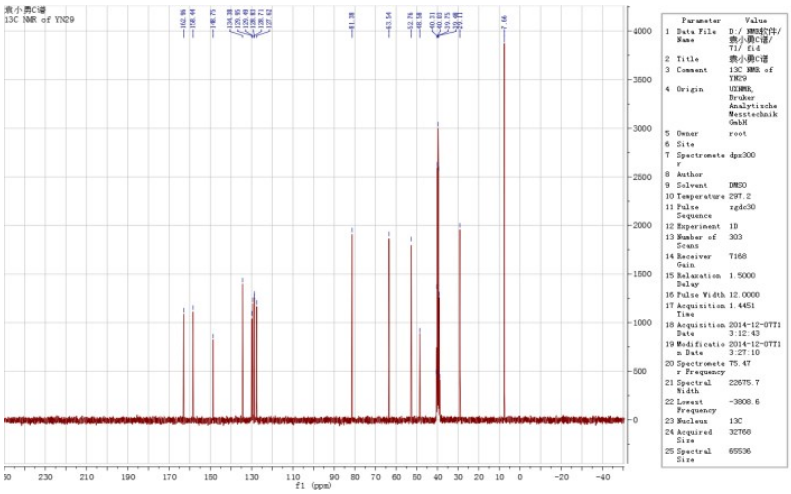

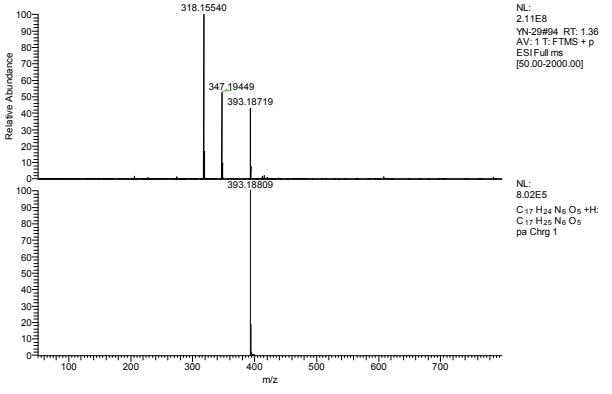

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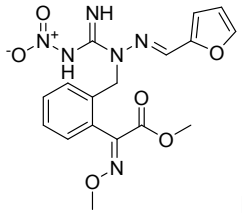

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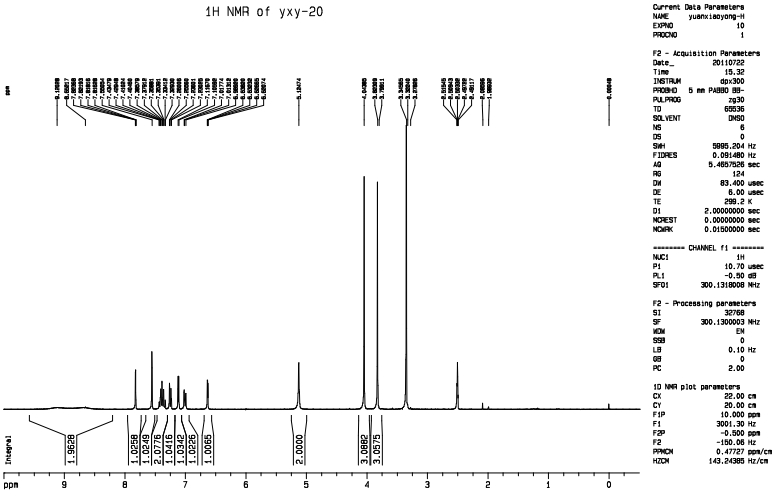

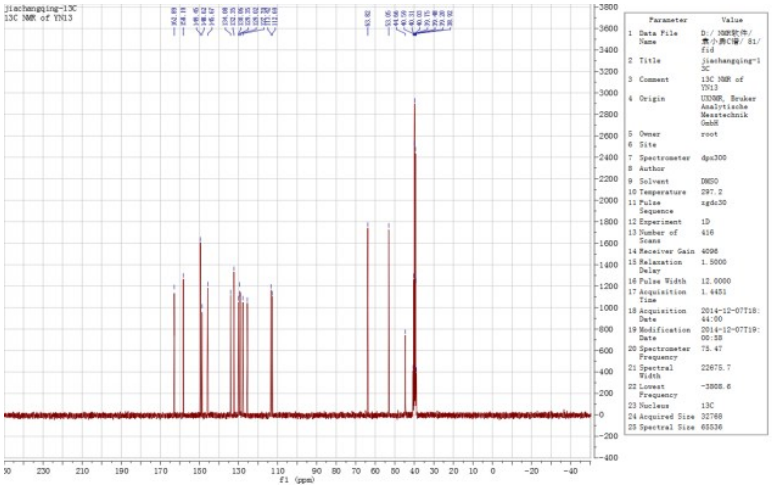

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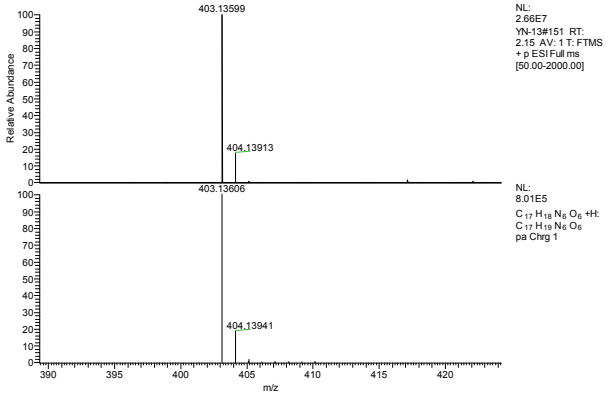

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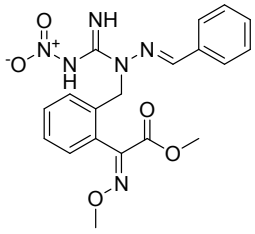

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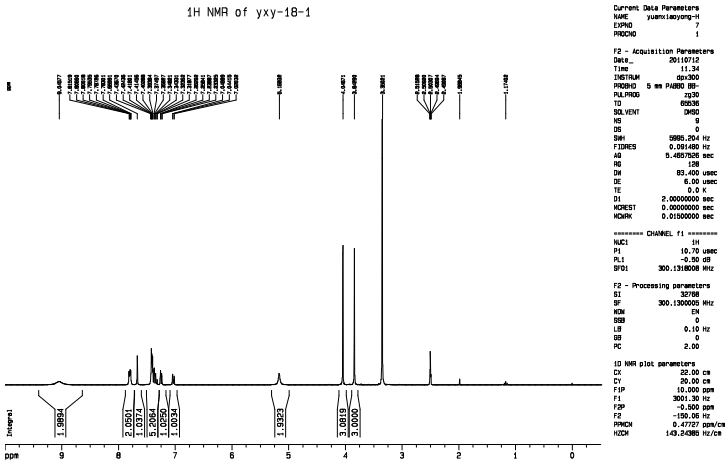
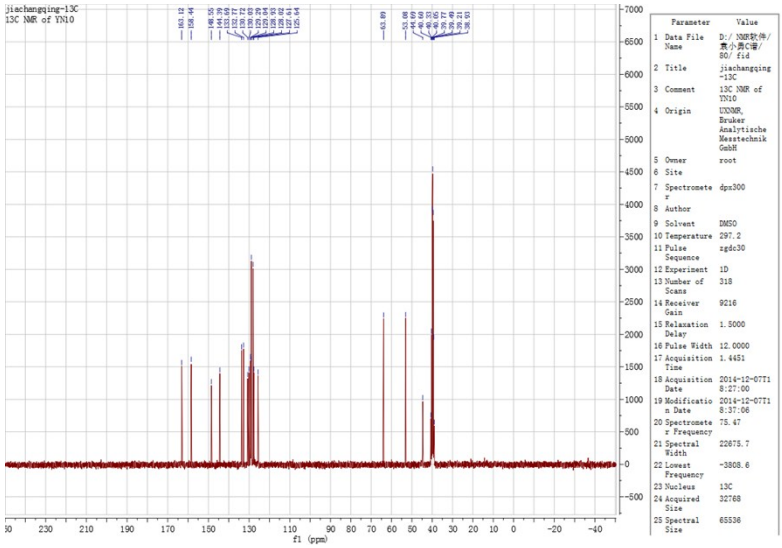
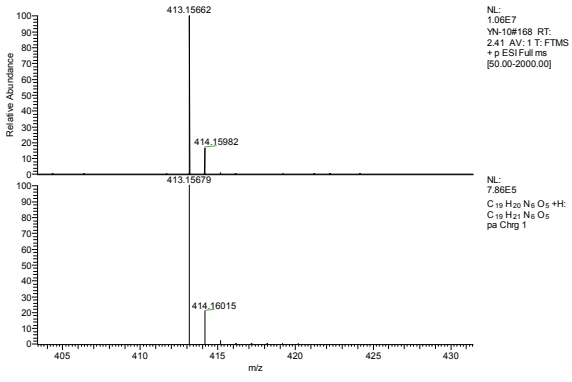
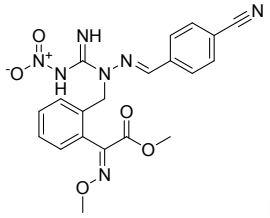


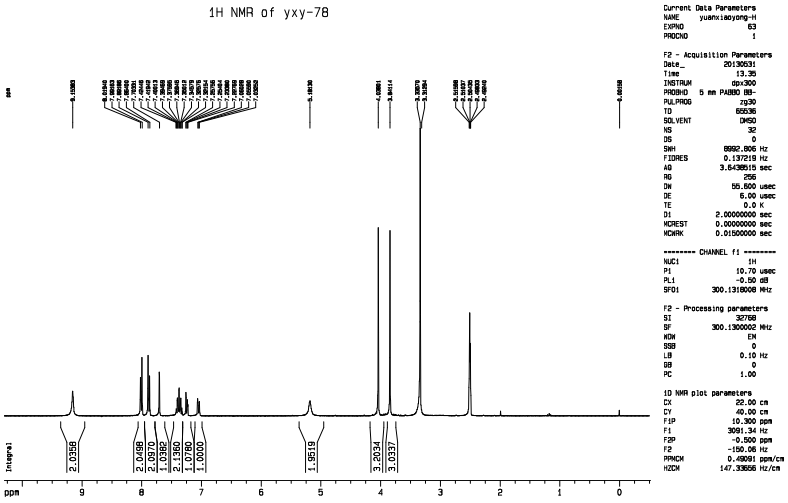


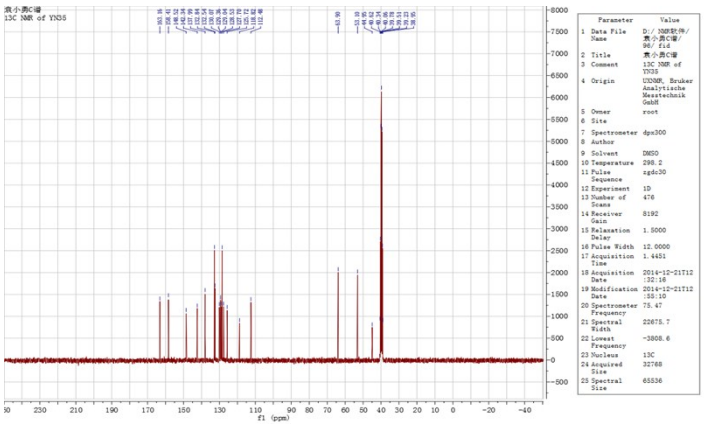


6-09



MW 437.1448





Parameter	Value
1 Data File Name	D:/NMR软件/黄小惠C谱/96/fid
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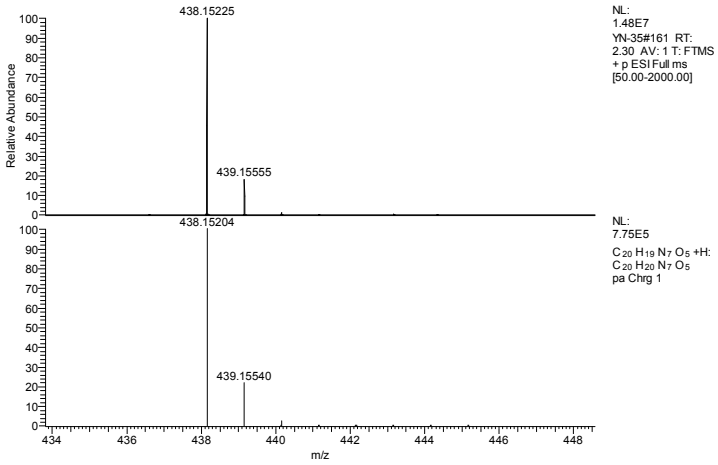
3 Comment	13C NMR of YN35
4 Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5 Owner	root
6 Site	
7 Spectrometer	dpx300
8 Author	
9 Solvent	DMSO
10 Temperature	298.2
11 Pulse Sequence	zgdc30
12 Experiment	1D
13 Number of Scans	476
14 Receiver Gain	8192
15 Relaxation Delay	1.5000
16 Pulse Width	12.0000
17 Acquisition Time	1.4451
18 Acquisition Date	2014-12-21T12:32:16
19 Modification Date	2014-12-21T12:55:10
20 Spectrometer Frequency	75.47
21 Spectral Width	22675.7
22 Lowest Frequency	-3808.6
23 Nucleus	13C
24 Acquired Size	32768
25 Spectral Size	65536



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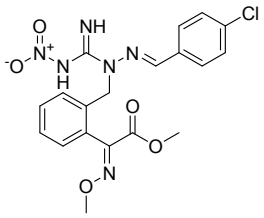
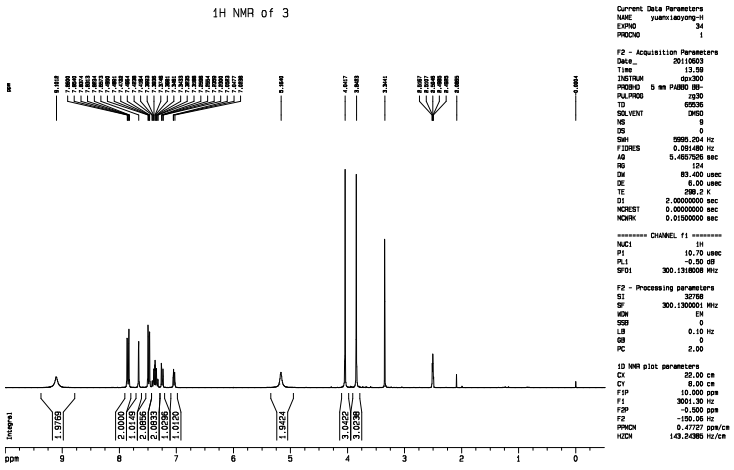
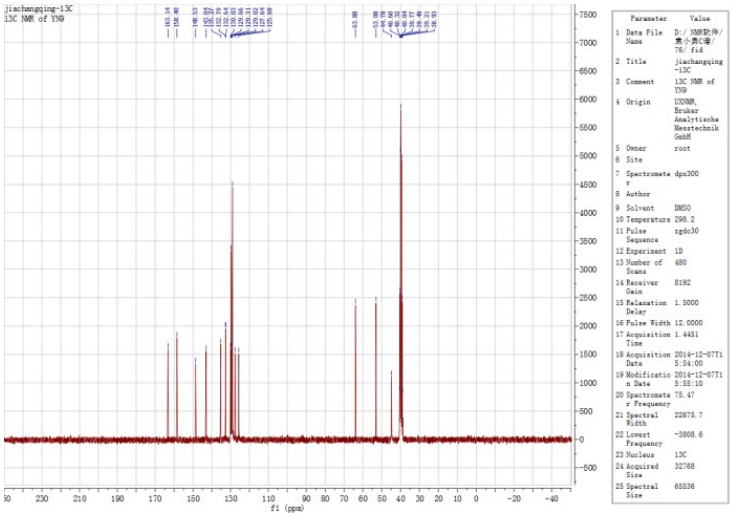
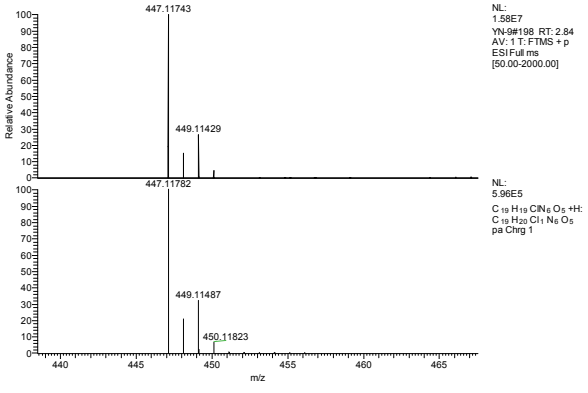


MW 446.1105







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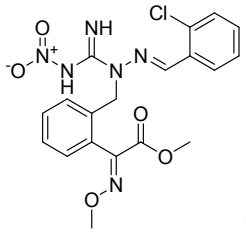

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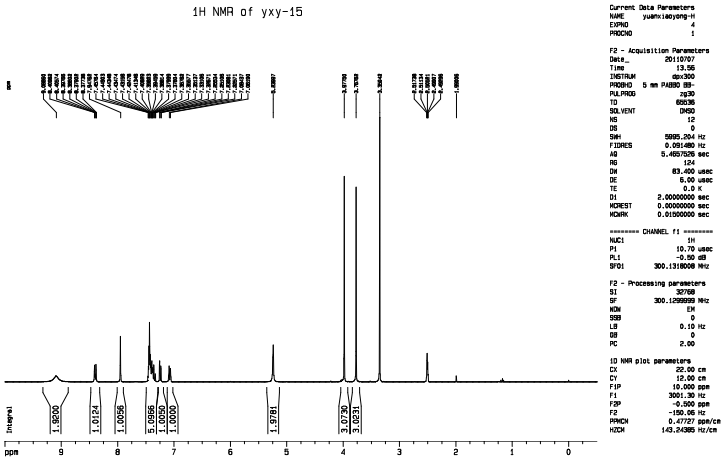

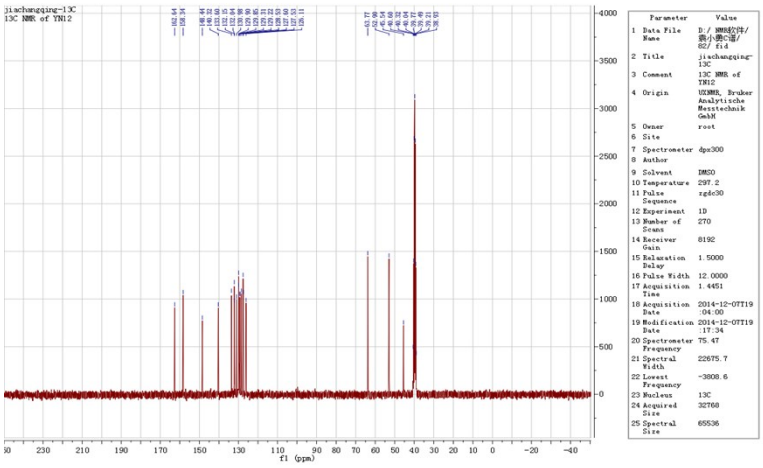

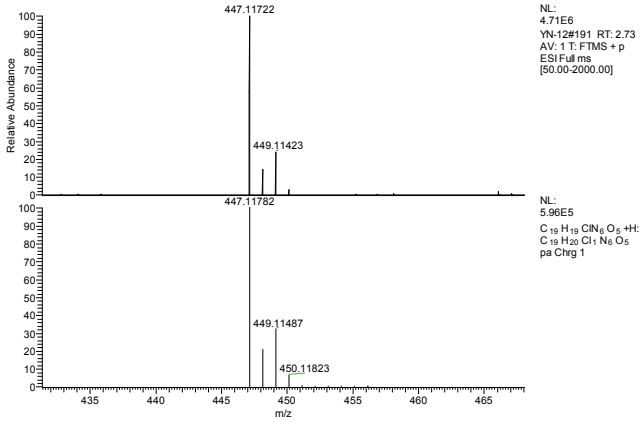

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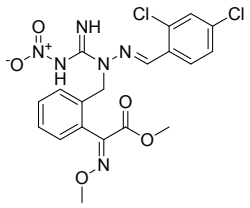
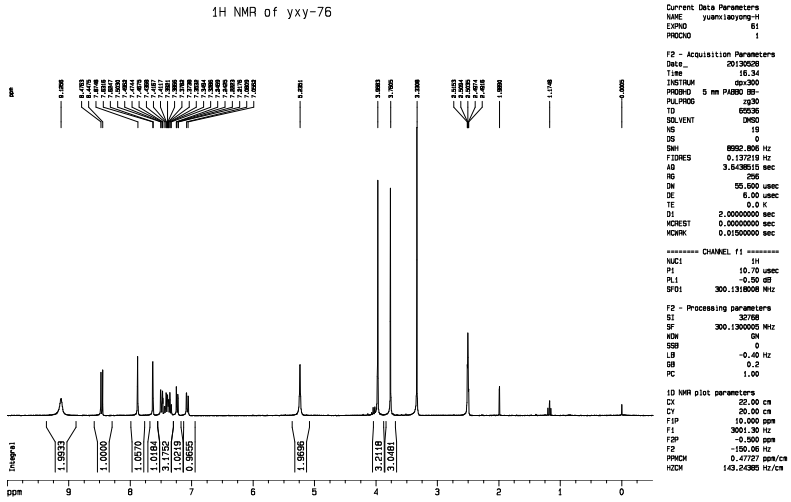
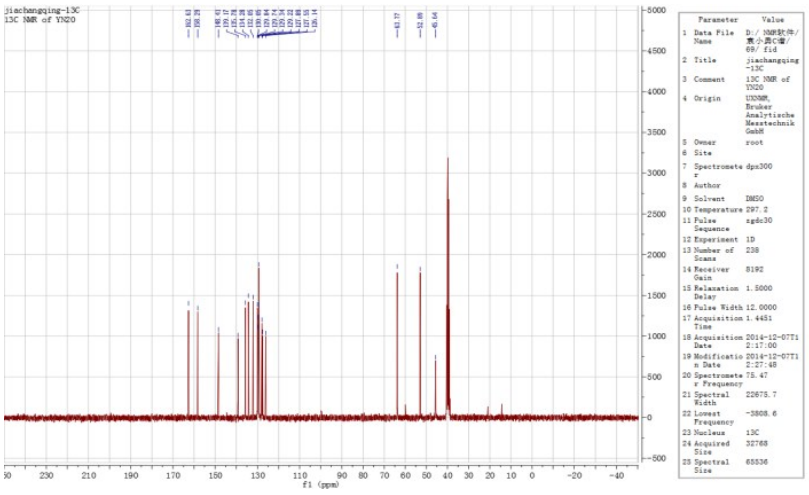
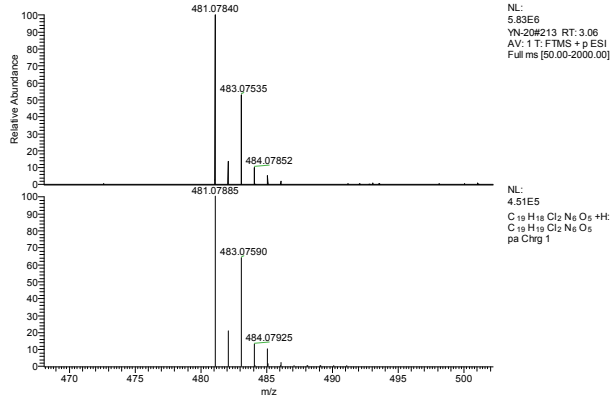


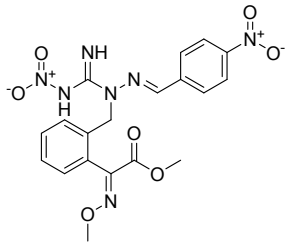
MW 480.0716



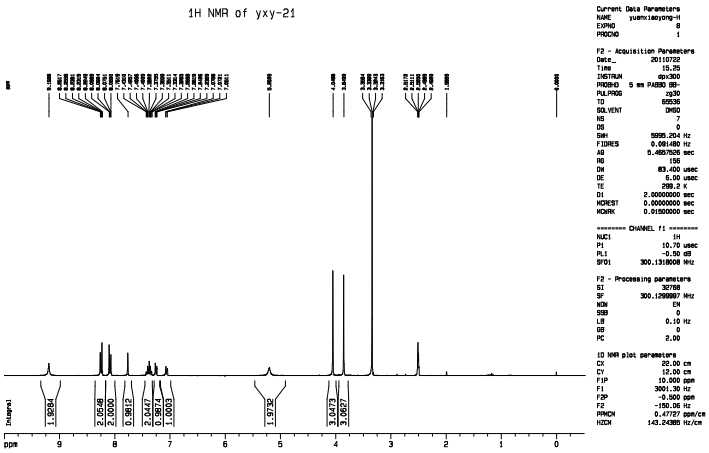


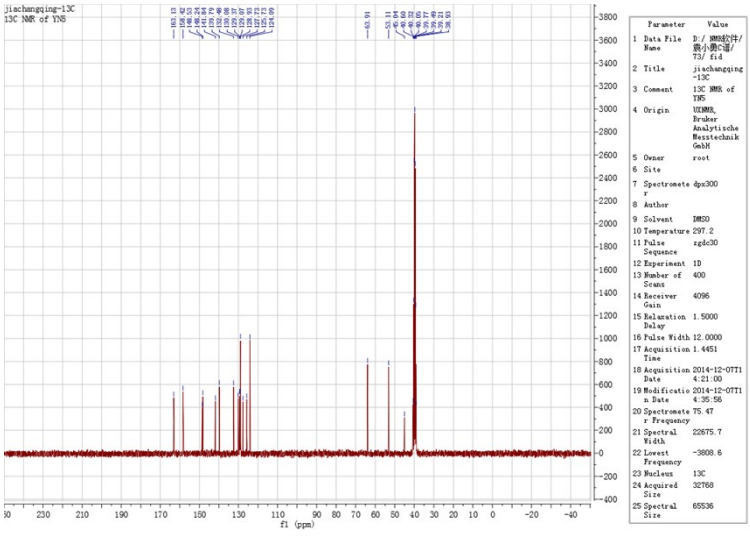


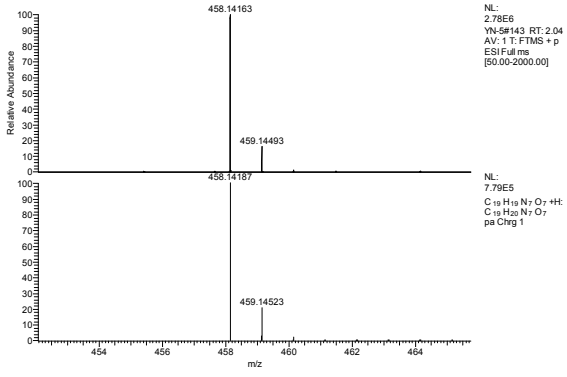
6-13



MW 457.1346







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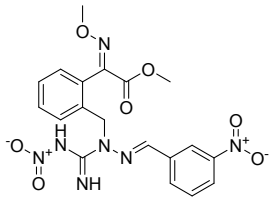
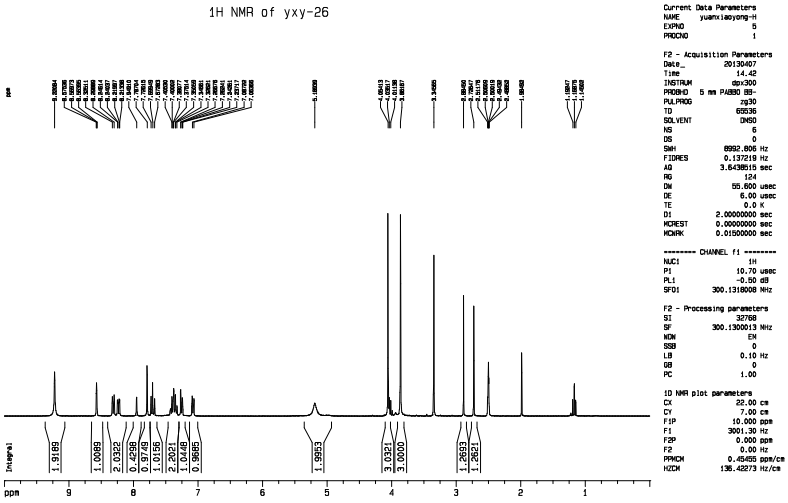
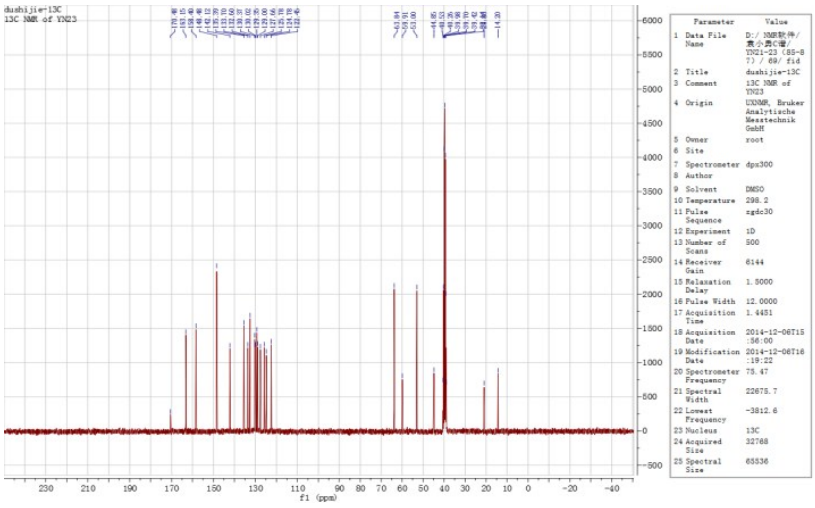
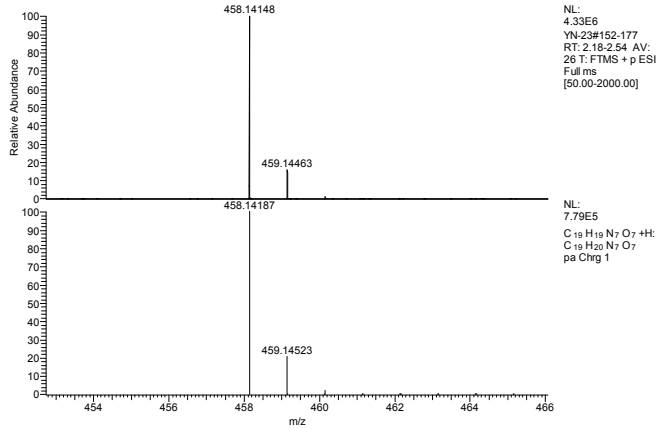
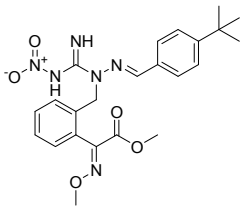


MW 457.1346

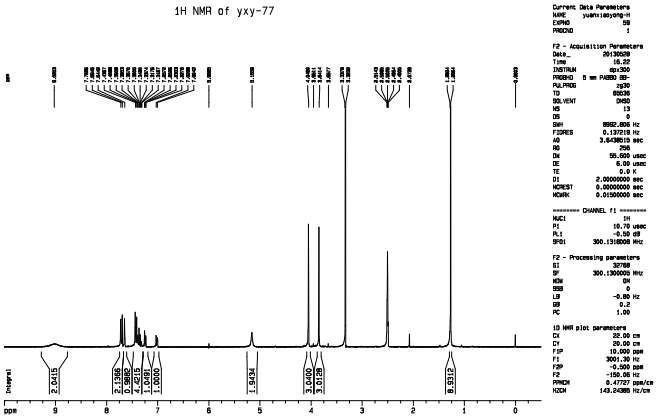








MW 468.2121


1H NMR of yxy-77
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NAME yuanxiaoyong-H
EXPNO 59
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130509
Time 16.22
INSTRUM dpx300
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 13
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6453615 sec
RG 256
DW 55.600 usec
DE 6.00 usec
TE 0.0 K
D1 2.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 10.70 usec
PL1 -0.00 dB
SFO1 300.1318008 MHz
F2 - Processing parameters
SI 32768
SF 300.1300005 MHz
WDW EM
SSB 0
LB -0.80 Hz
GB 0.2
PC 1.00
1D NMR plot parameters
CX 22.00 cm
CY 20.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.000 ppm
F2 -150.36 Hz
PPMCM 0.47727 ppm/cm
HZCM 143.24285 Hz/cm
Integral
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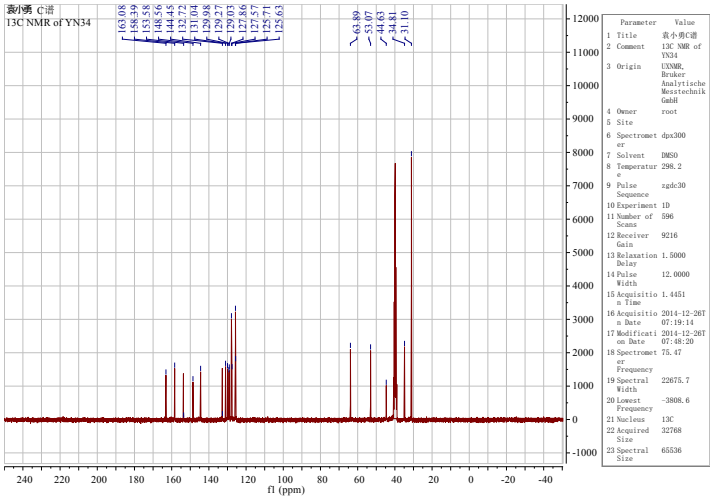
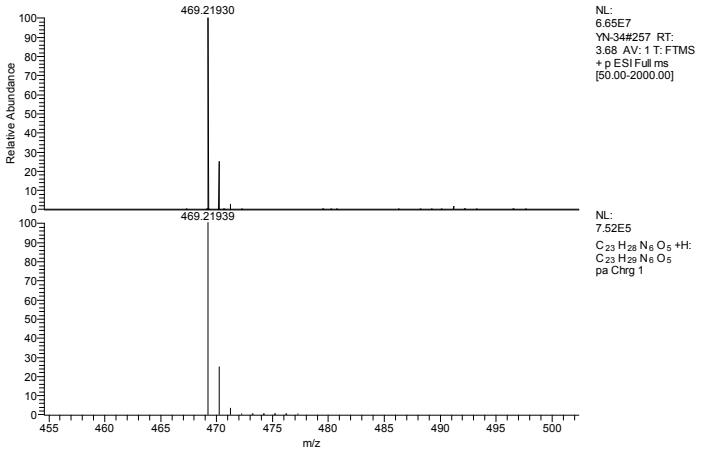
1.0000
1.9434
3.0040
3.0128
8.5312
ppm


袁小勇 C谱
13C NMR of YN34
163.08
158.39
153.58
148.56
144.45
143.72
131.04
129.98
129.27
129.03
127.86
127.57
127.31
125.63
63.89
53.07
44.63
34.81
31.10
fl (ppm)
Parameter Value
1 Title 袁小勇C谱
2 Comment 13C NMR of YN34
3 Origin UXNMR, Bruker Analytische Messtechnik GmbH
4 Owner root
5 Site
6 Spectrometer dpx300
7 Solvent DMSO
8 Temperature 298.2
9 Pulse Sequence zgdc30
10 Experiment 1D
11 Number of Scans 596
12 Receiver Gain 9216
13 Relaxation Delay 1.5000
14 Pulse Width 12.0000
15 Acquisition Time 1.4451
16 Acquisition Date 2014-12-26T 07:19:14
17 Modification Date 2014-12-26T 07:48:20
18 Spectrometer Frequency 75.47
19 Spectral Width 22675.7
20 Lowest Frequency -3808.6
21 Nucleus 13C
22 Acquired Size 32768
23 Spectral Size 65536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m/z
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3.68 AV: 1 T: FTMS
+ p ESI Full ms
[50.00-2000.00]
469.21939
NL:
7.52E5
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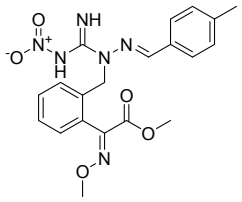
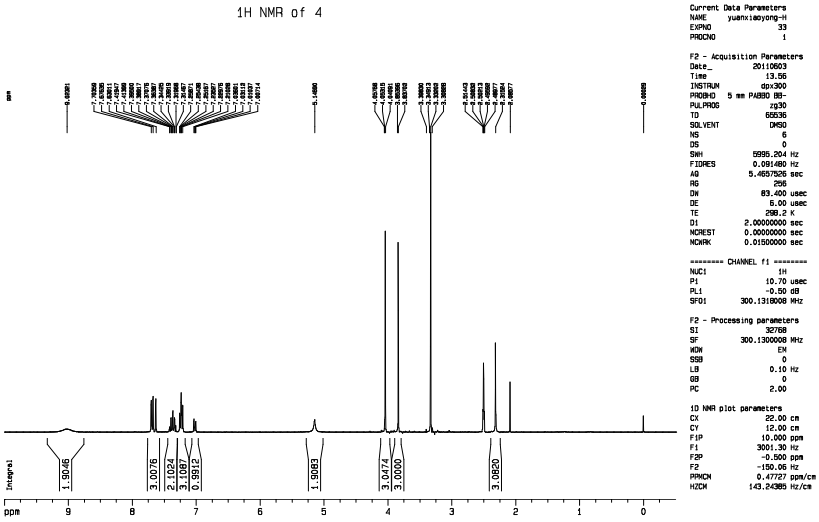
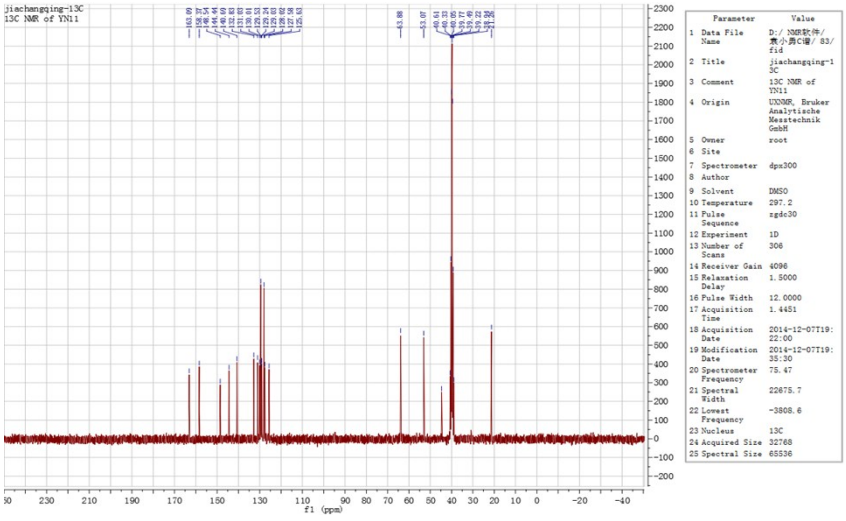
pa Chrg 1



MW 426.1652





	Parameter	Value
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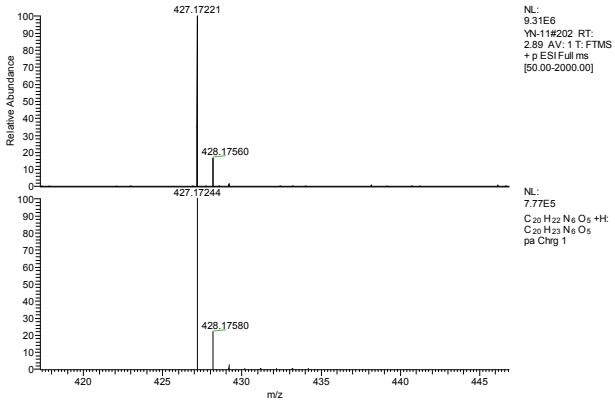
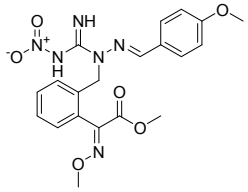
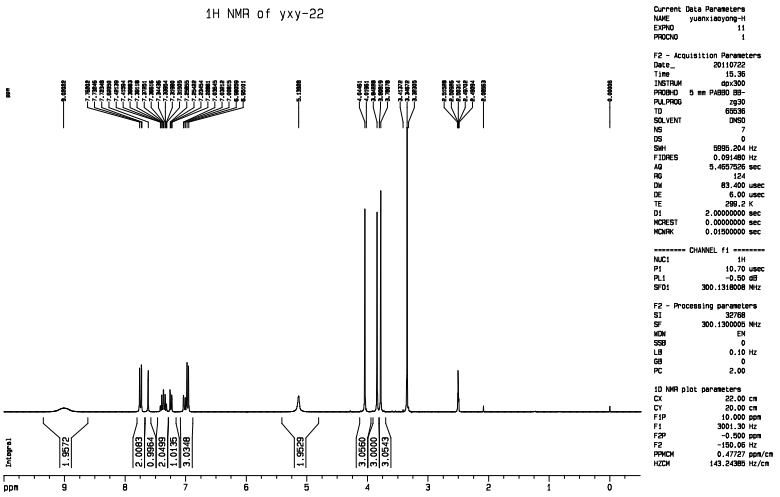
4	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
5	Owner	root
6	Site	
7	Spectrometer	dpx300
8	Author	
9	Solvent	DMSO
10	Temperature	297.2
11	Pulse Sequence	zgdc30
12	Experiment	1D
13	Number of Scans	306
14	Receiver Gain	4096
15	Relaxation Delay	1.5000
16	Pulse Width	12.0000
17	Acquisition Time	1.4451
18	Acquisition Date	2014-12-07T19:22:00
19	Modification Date	2014-12-07T19:35:30
20	Spectrometer Frequency	75.47
21	Spectral Width	22675.7
22	Lowest Frequency	-3808.6
23	Nucleus	13C
24	Acquired Size	32768
25	Spectral Size	65536

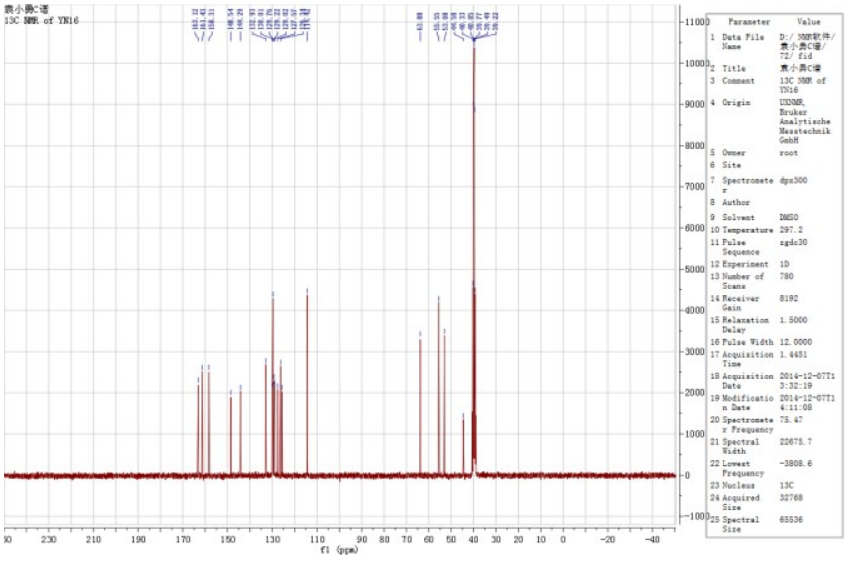


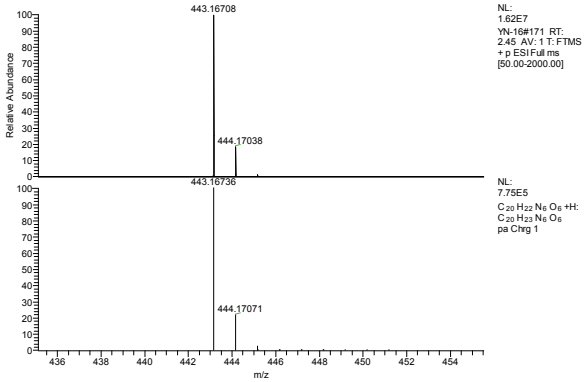
6-17



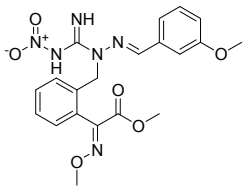
MW 442.1601



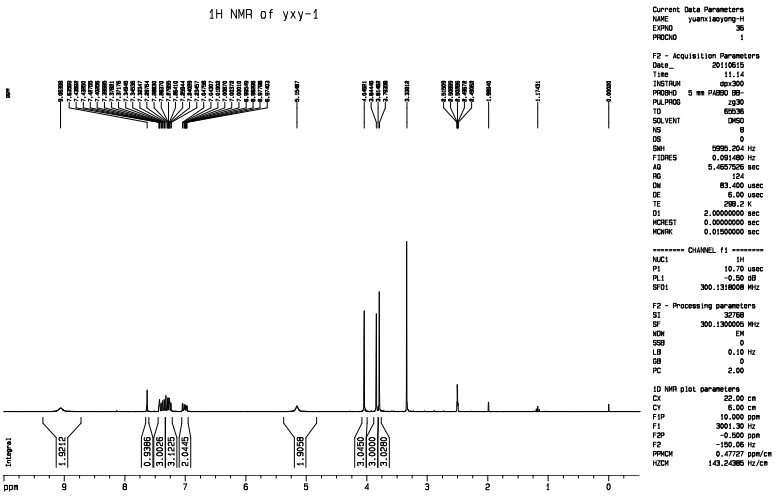


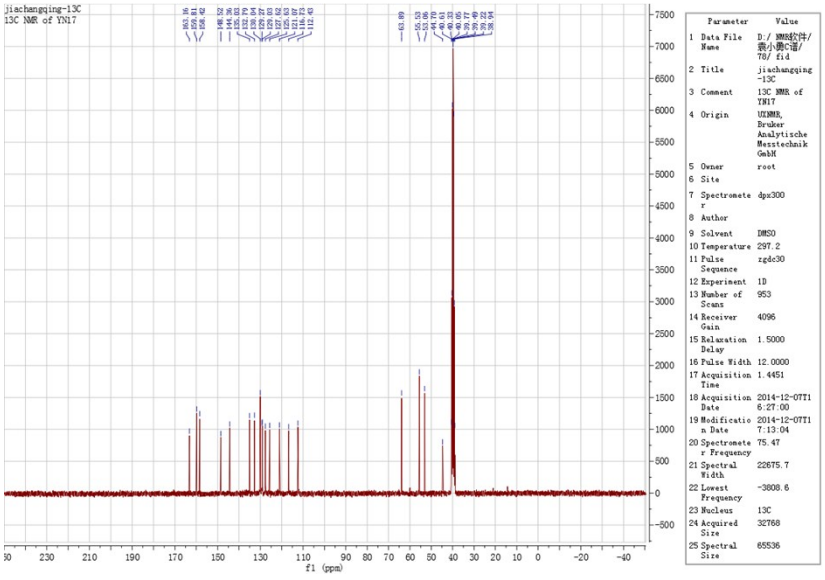


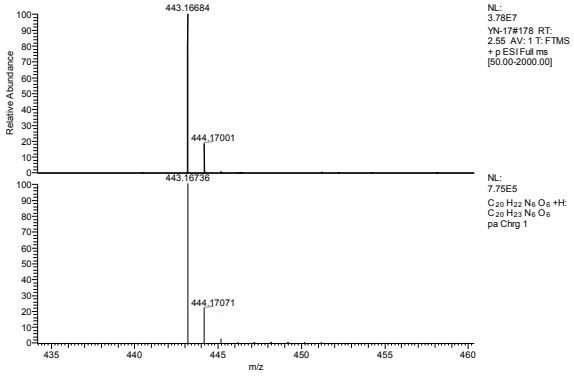
6-18

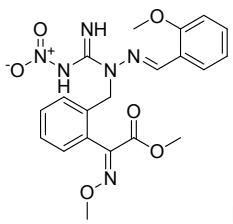


MW 442.1601

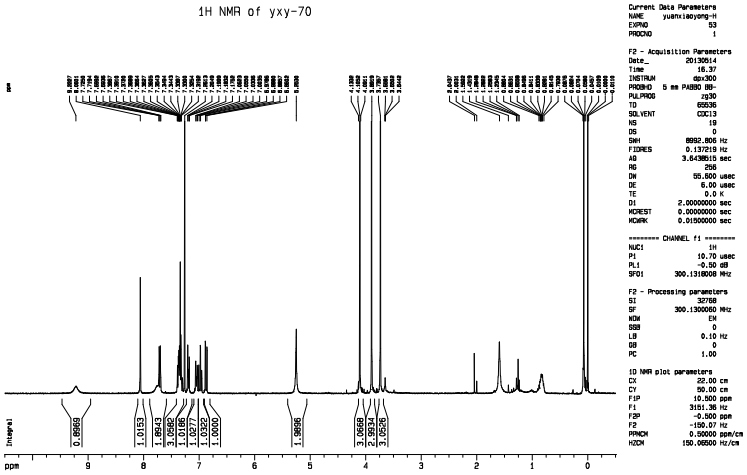


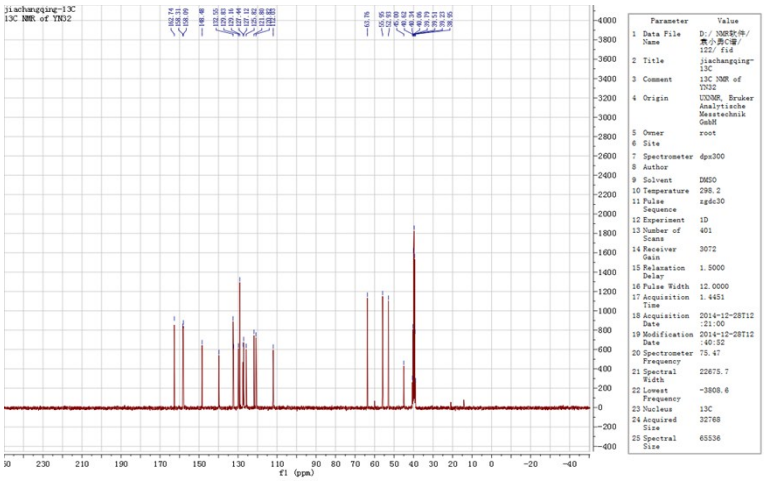


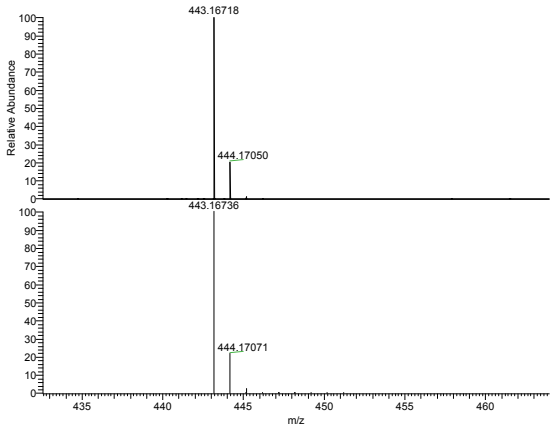




MW 442.1601







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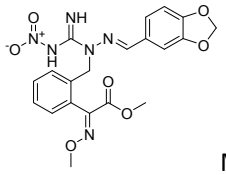
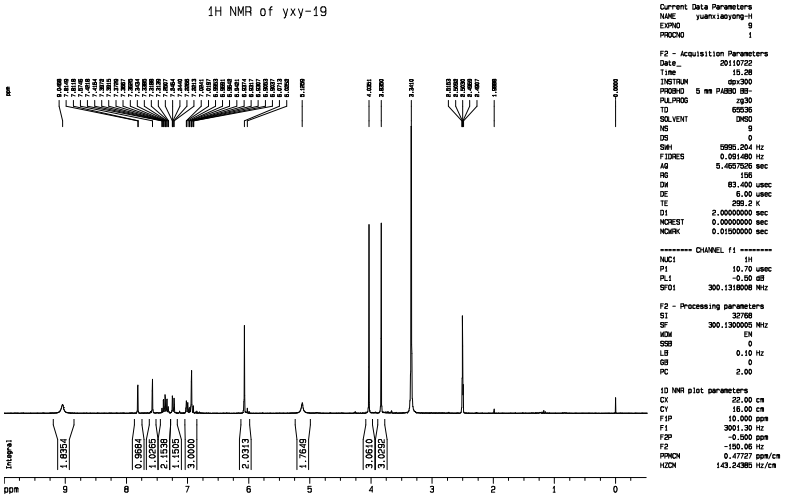
2.58 AV: 1 T: FTMS
+ p ESI Full ms
[50.00-2000.00]

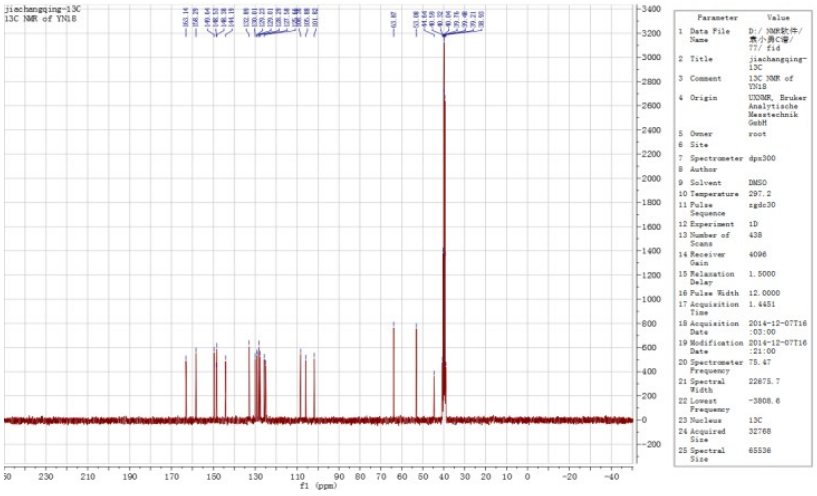
NL:
7.75E5
$C_{20}H_{22}N_6O_6$ +H:
$C_{20}H_{23}N_6O_6$
pa Chrg 1

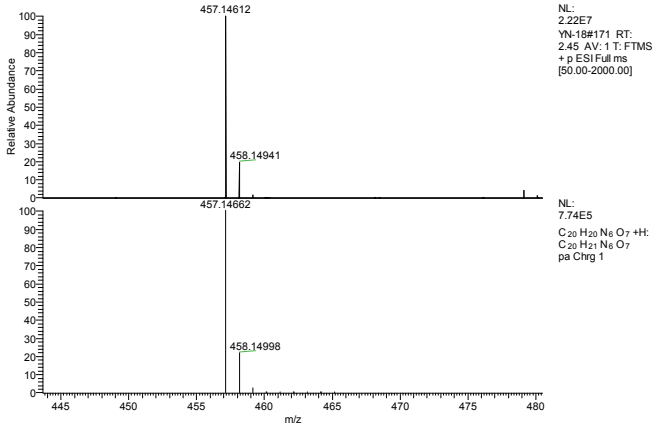
6-20



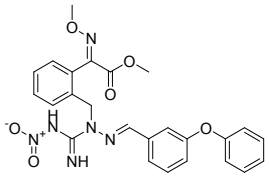
MW 456.1393



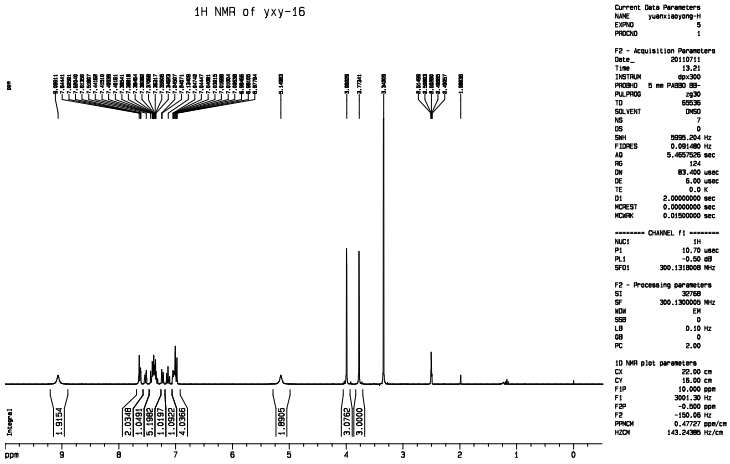


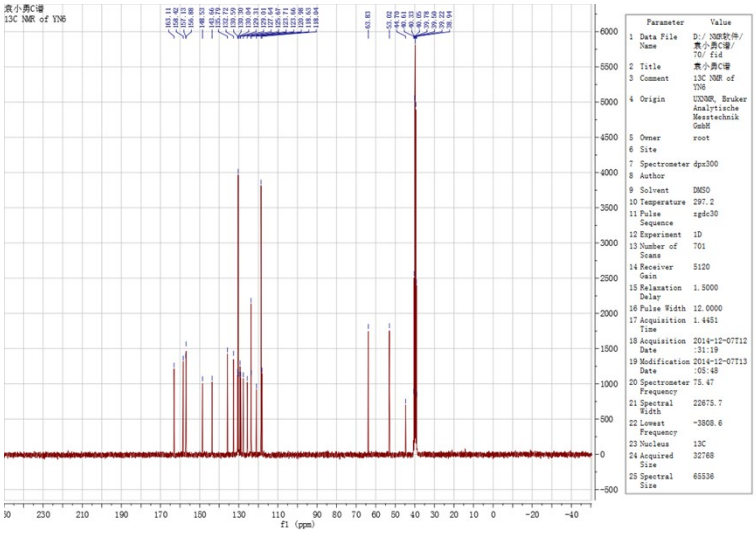


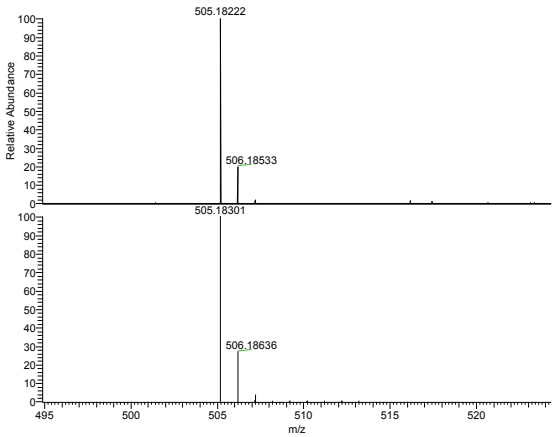
6-21



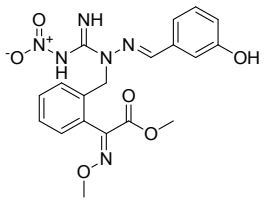
MW 504.1757



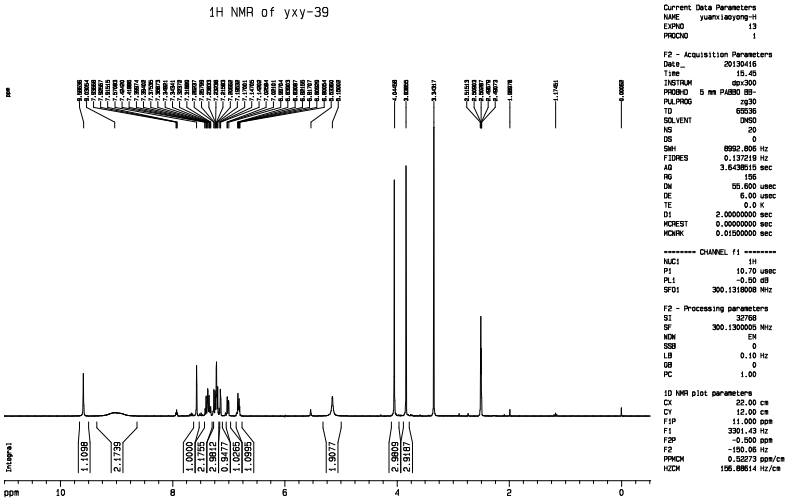


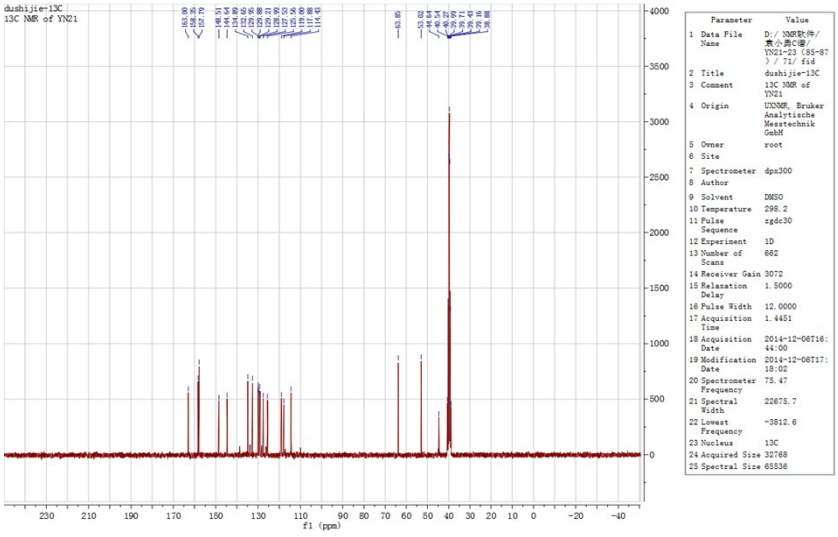


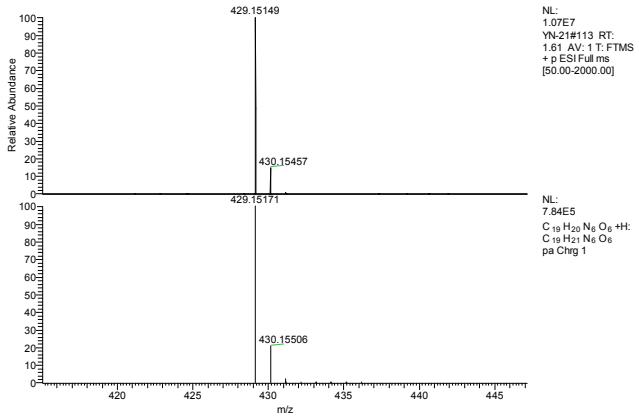
6-22



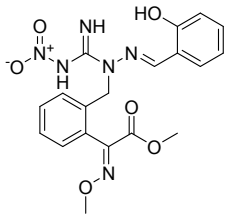
MW 428.1444



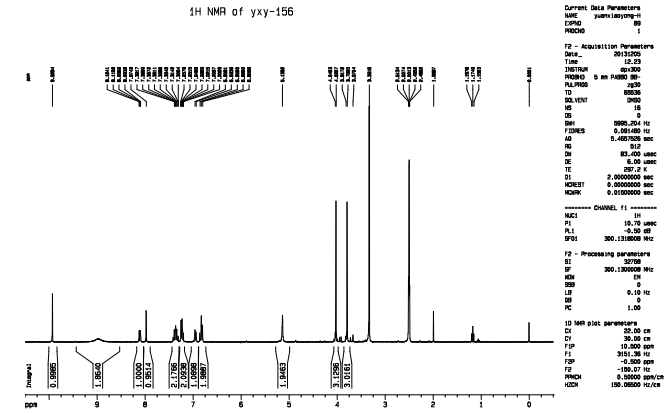


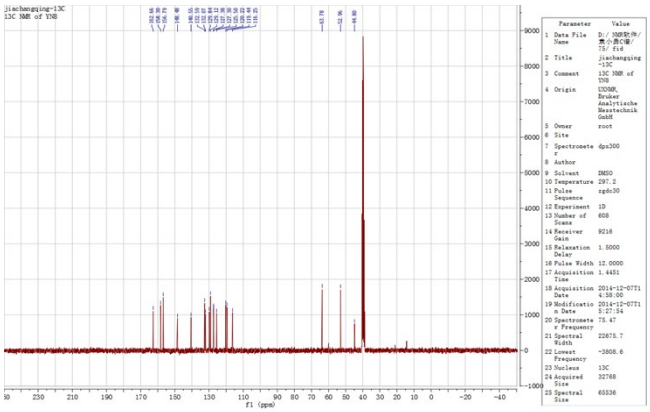


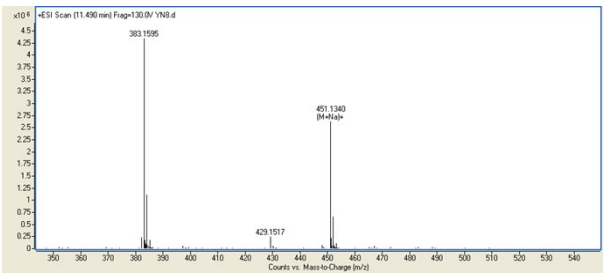
6-23

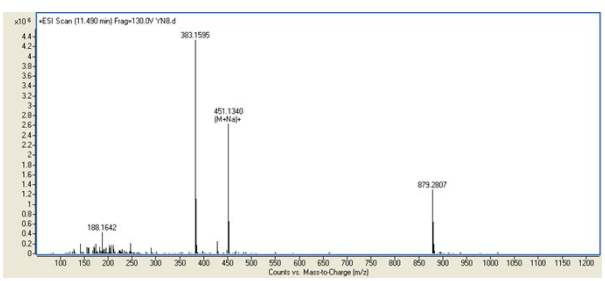


MW 428.1444

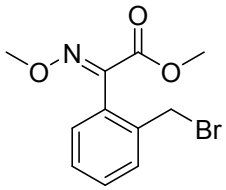




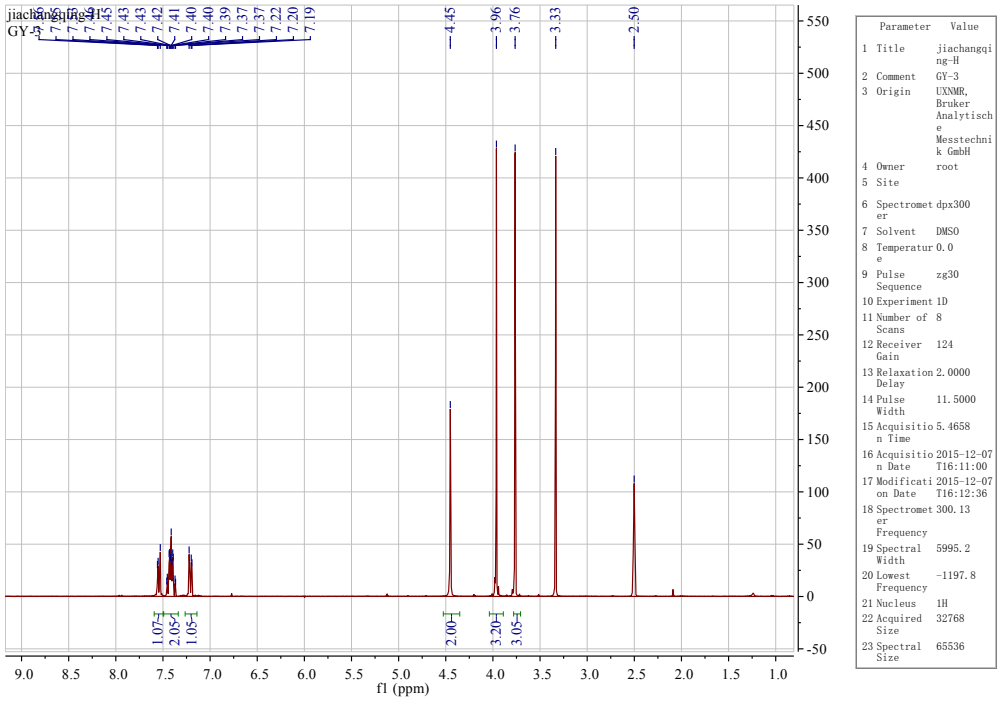




(E)-methyl 2-(2-(bromomethyl)phenyl)-2-(methoxyimino)acetate



^{1}H NMR (300 MHz, DMSO-d_6) δ 7.59 – 7.50 (m, 1H), 7.49 – 7.34 (m, 2H), 7.26 – 7.14 (m, 1H), 4.45 (s, 2H), 3.96 (s, 3H), 3.76 (s, 3H).



^{1}H NMR date of (E)-methyl 2-(2-(bromomethyl)phenyl)-2-(methoxyimino)acetate in References 19:

^{1}H NMR (600 MHz, $CDCl_3$): 3.86 (3H,s, -COOMe), 4.04 (3H, s, N-OCH3), 4.31 (2H, s, -CH2-), 7.13 (1H,dd, J_1 =7.8 Hz, J_2= 1.2 Hz, 3-ArH), 7.35-7.40 (2H, m, Ar-H),7.46 (1H, dd, J_1= 7.8 Hz, J_2= 0.6 Hz, 6-ArH).