

Supporting information

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

Xiaoyong Yuan,^{§,a,b} Changqing Jia,^{§,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

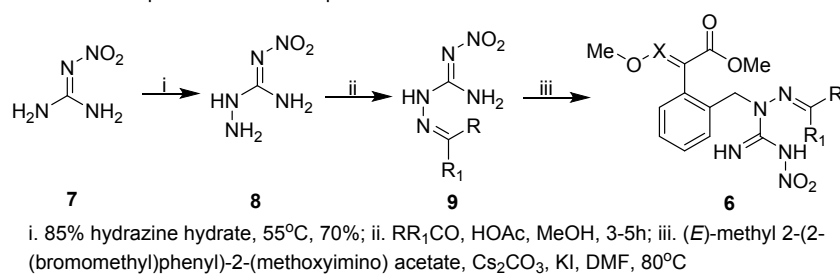
c. Institute of Plant Protection, Chinese Academy of Agricultural Sciences, Beijing 100193, China

[§] 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. Preparation of title compounds



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 °C under stirring, 85% hydrazine hydrate (0.216 mol) was added dropwise to the mixture, the reaction was allowed to stir 15 minutes at 55°C. At this point, the solid was all dissolved in the water, then the solution was quickly cooled to about 20°C, 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°C, yield 70%. 1H 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°C, yield 80%. 1H 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°C, yield 82%. 1H 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°C, yield 75%. 1H 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°C, yield 70%. 1H 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°C,

yield 80%. ¹H 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°C, yield 75%. ¹H 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-(Furan-2-ylmethylene)-N-nitrohydrazinecarboximidamide(9-07): yellowish solid, mp 222 - 224°C, yield 87%. ¹H 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°C, yield 86%. ¹H 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°C, yield 85%. ¹H 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°C, yield 92%. ¹H 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°C, yield 90%. ¹H 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°C, yield 92%. ¹H 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°C, yield 95%. ¹H 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°C, yield 91%. ¹H 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°C, yield 89%. ¹H 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°C, yield 84%. ¹H 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°C, yield 92%. ¹H 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°C, yield 90%. ¹H 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°C, yield 88%. ¹H 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 °C, yield 88%. ¹H 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).

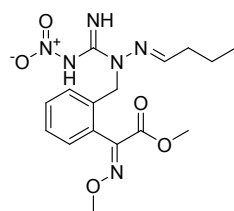
N-Nitro-2-(3-phenoxybenzylidene)hydrazinecarboximidamide(9-21): white solid, mp 211 - 213 °C, yield 90%. ¹H NMR (300 MHz, DMSO-*d*₆) δ 7.00 - 7.74 (m, 9H), 8.16 (s, 1H), 8.65 (brs, 1H), 8.84 (brs, 1H), 11.85 (s, 1H).

2-(3-Hydroxybenzylidene)-N-nitrohydrazinecarboximidamide(9-22): white solid, mp 210 - 212 °C, yield 90%. ¹H 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).

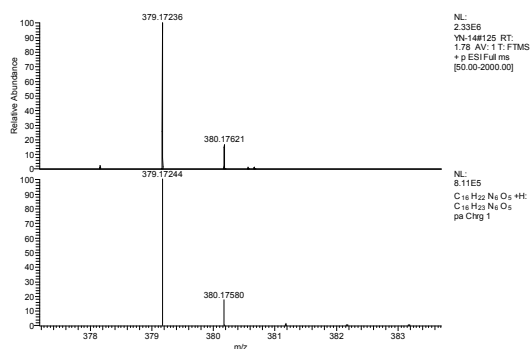
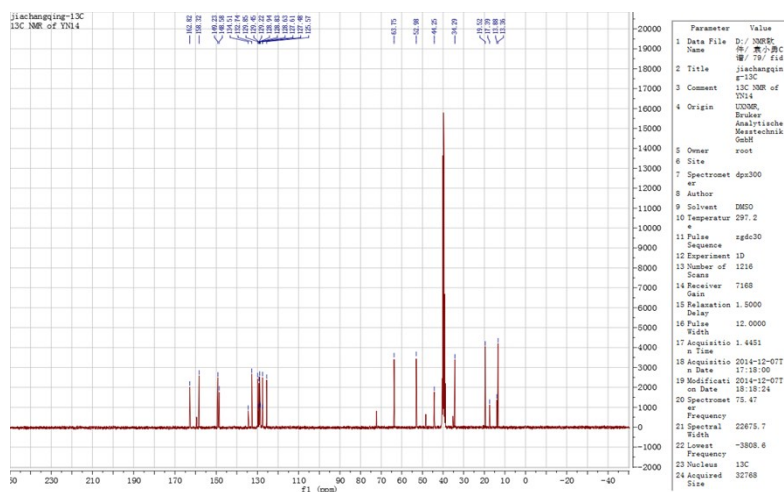
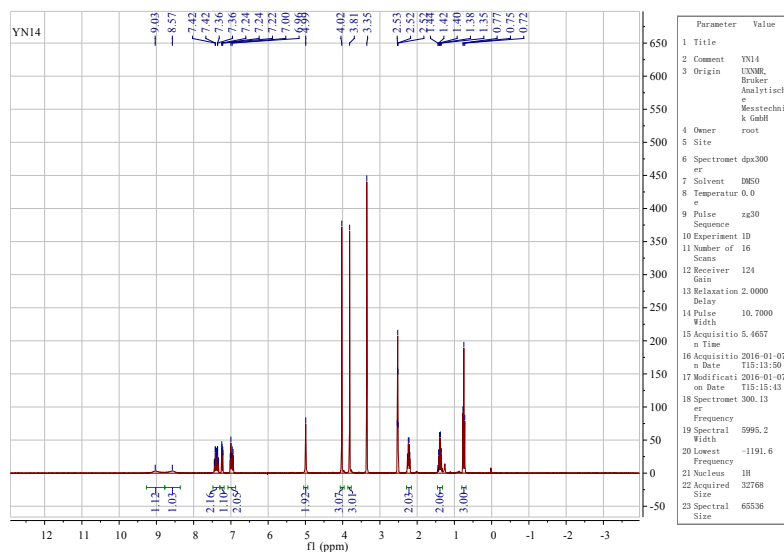
2-(2-Hydroxybenzylidene)-N-nitrohydrazinecarboximidamide(9-23): yellow solid, mp > 300 °C, yield 89%. ¹H NMR (300 MHz, DMSO-*d*₆) δ 6.82 - 8.04 (m, 4H), 8.47 (s, 1H), 8.78 (brs, 2H), 10.02 (s, 1H), 11.87 (s, 1H).

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

6-01

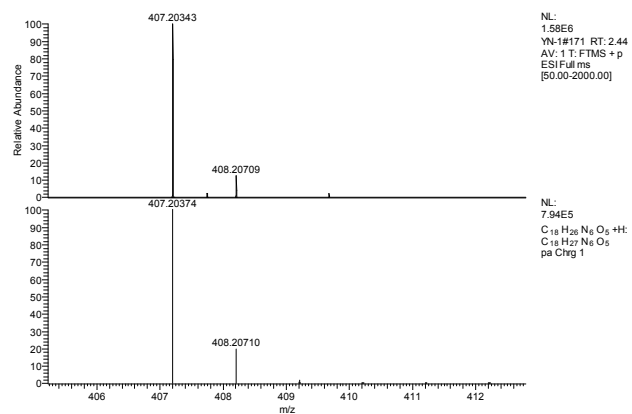
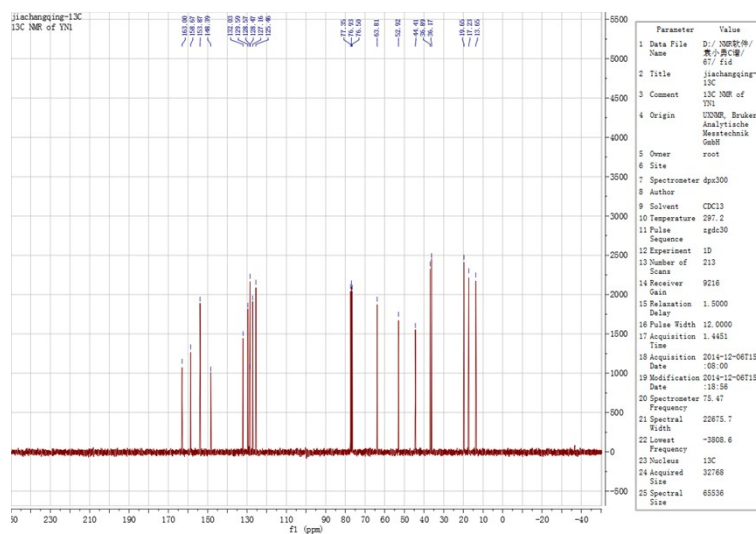
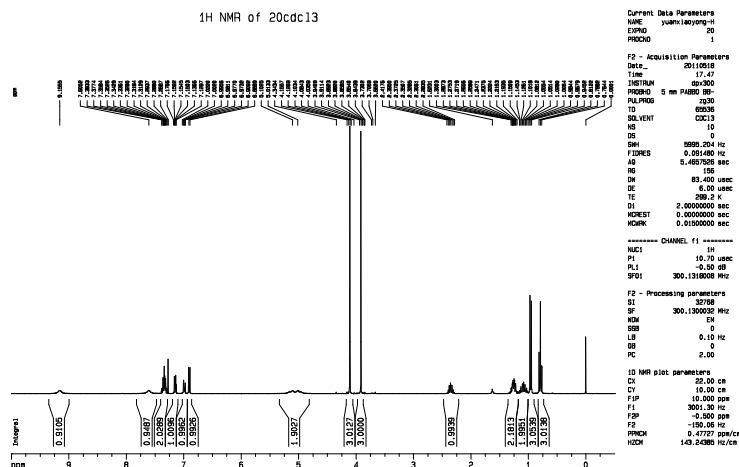


MW 378.1652

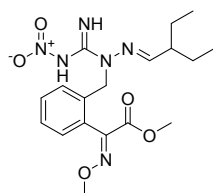


CC(C)C/C=N/N1C(=N)C([N+](=O)[O-])=NC1C2=CC=CC=C2C(=O)OC(=O)C2

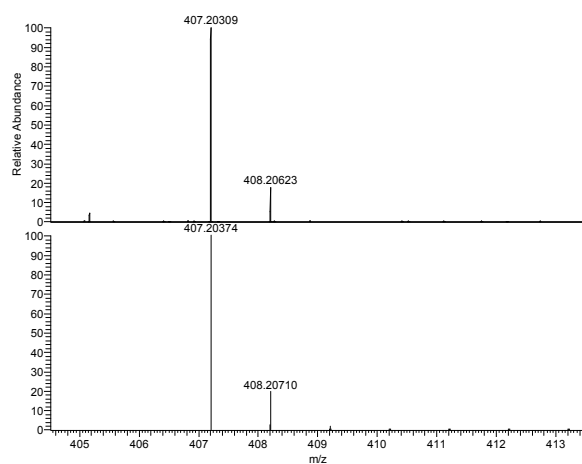
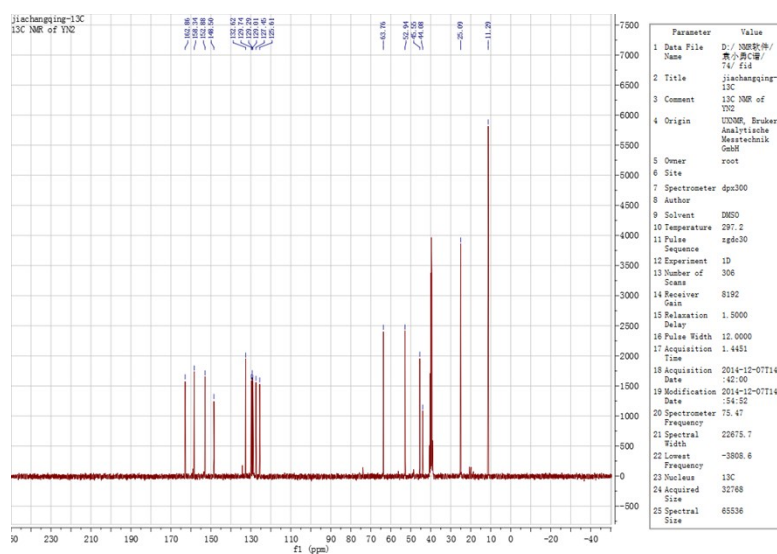
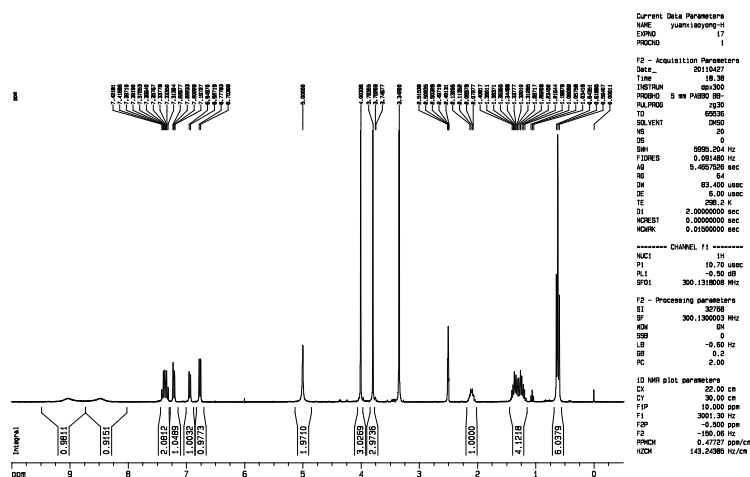
¹H NMR of 20cdc13



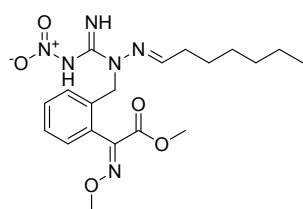
6-03



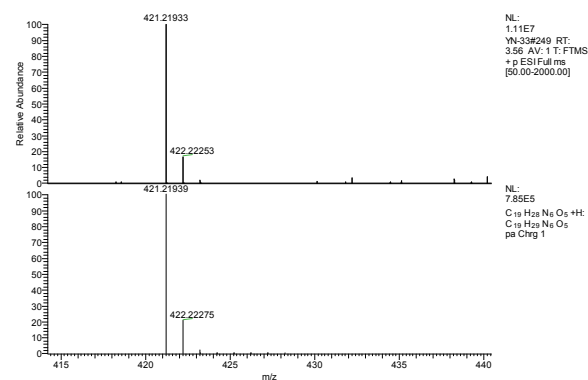
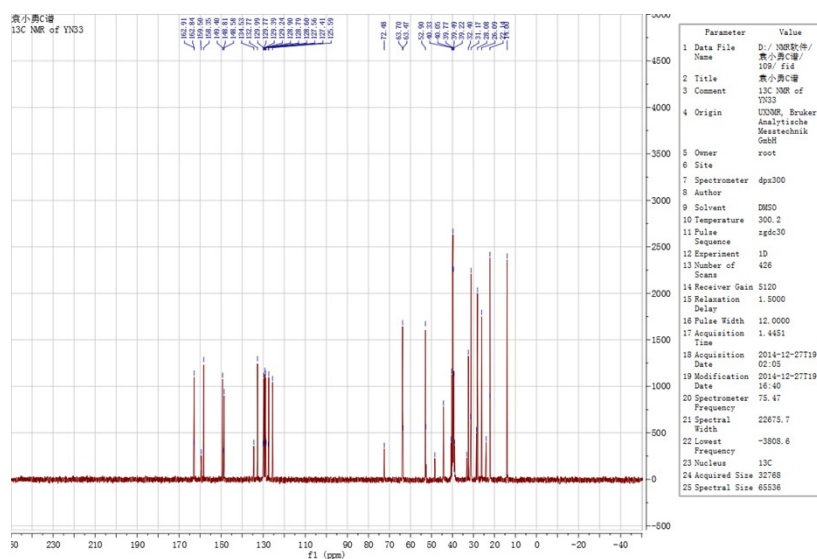
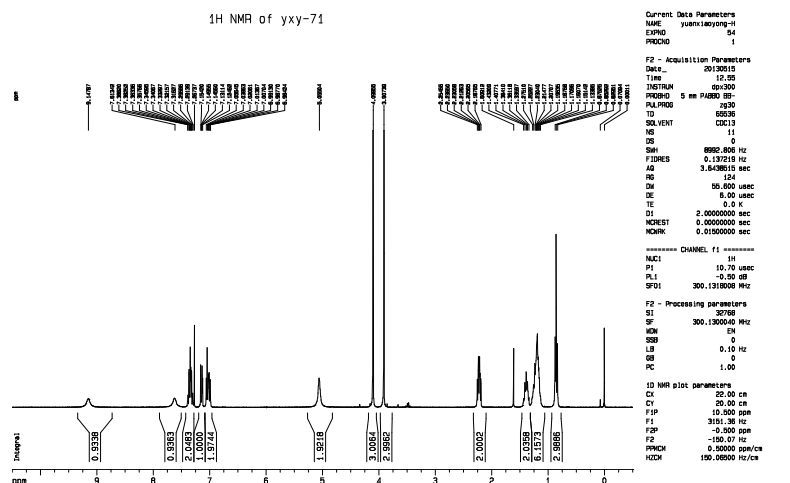
MW 406.1965



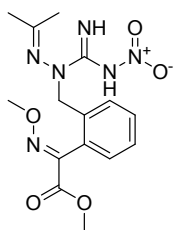
6-04



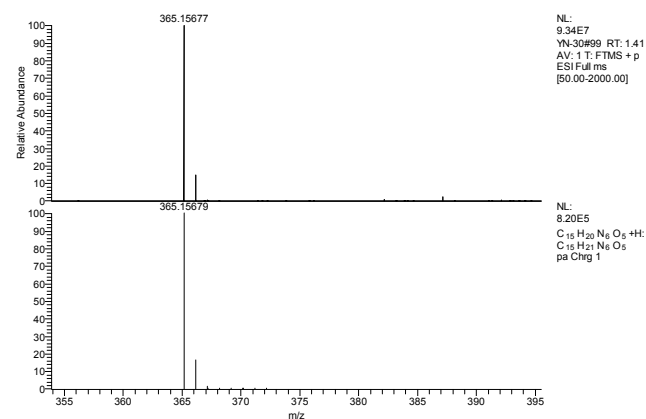
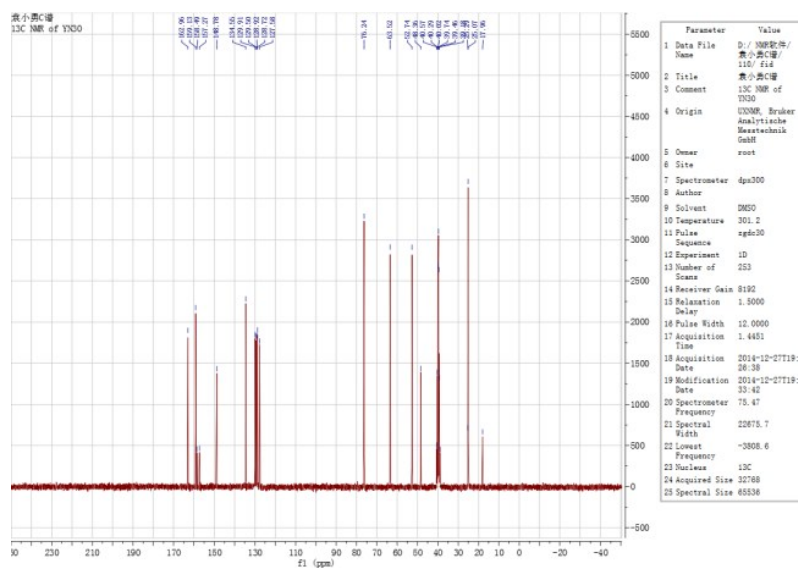
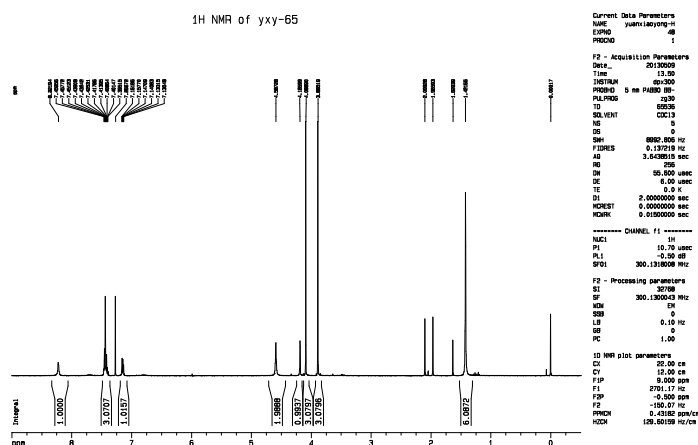
MW 420.2121



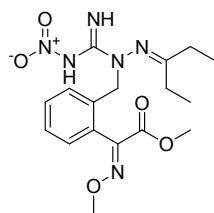
6-05



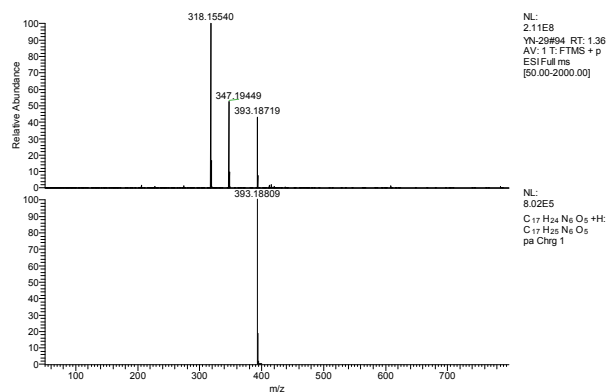
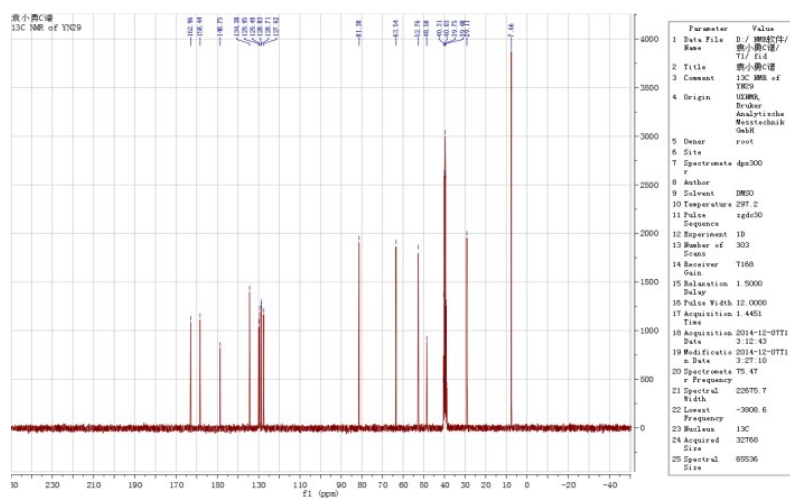
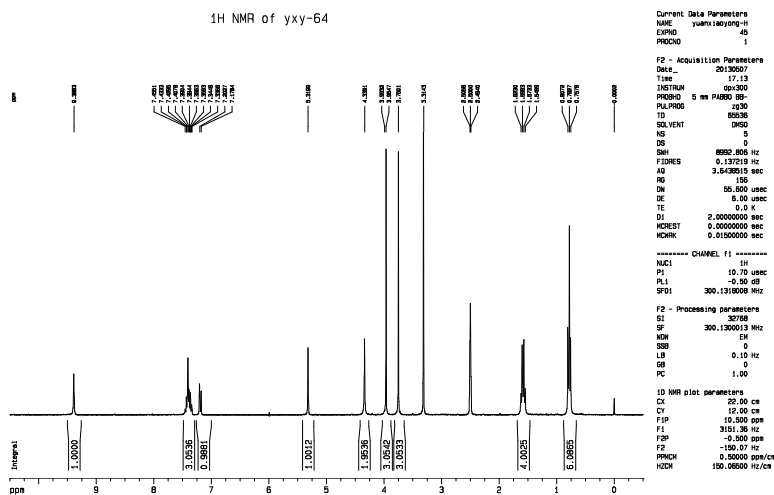
MW 364.1495



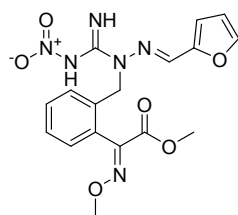
6-06



MW 392.1808

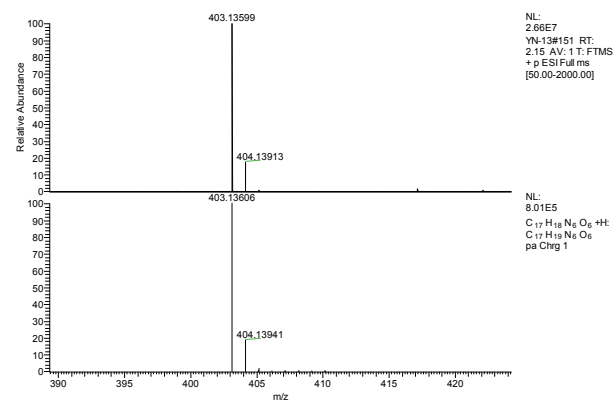
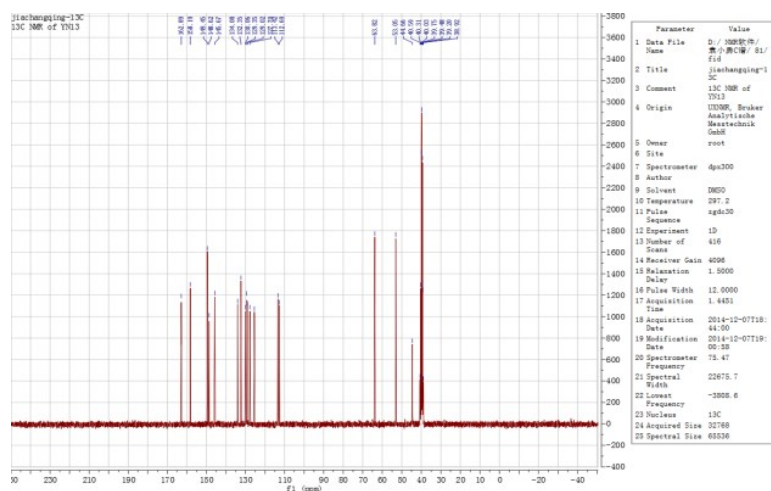
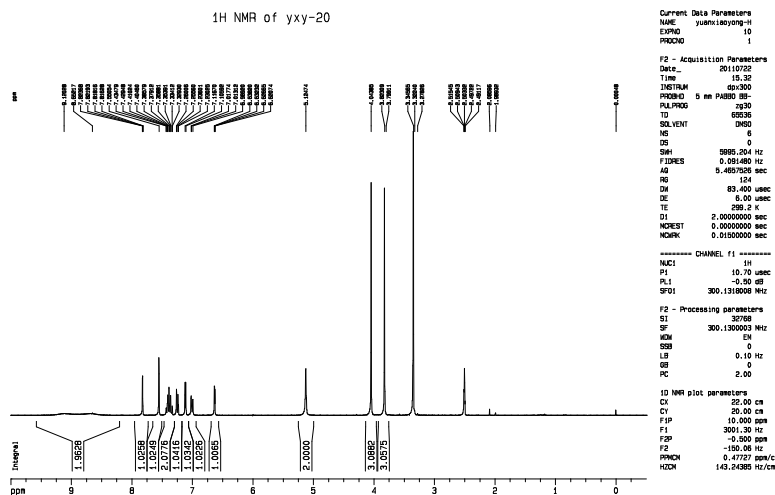


6-07

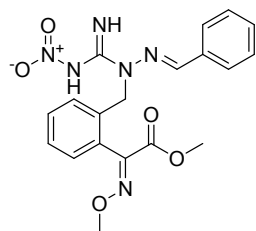


MW 402.1288

¹H NMR of yxy-20

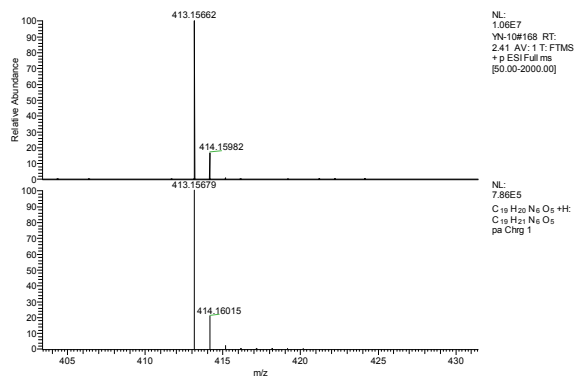
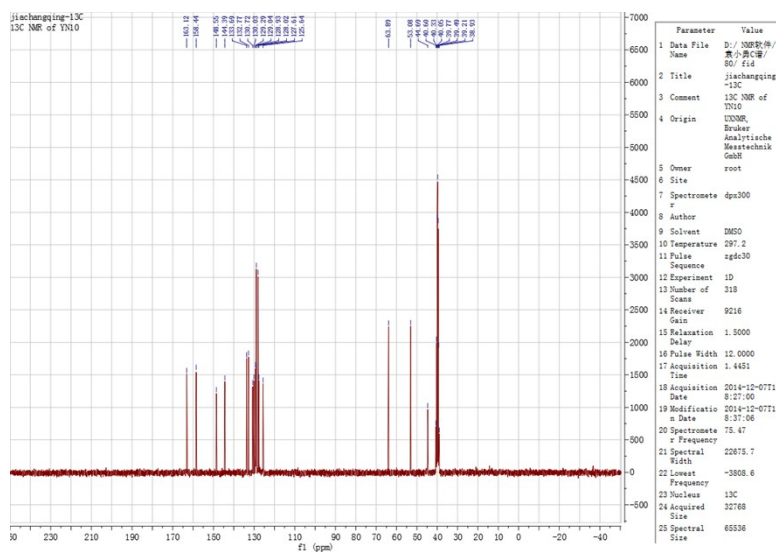
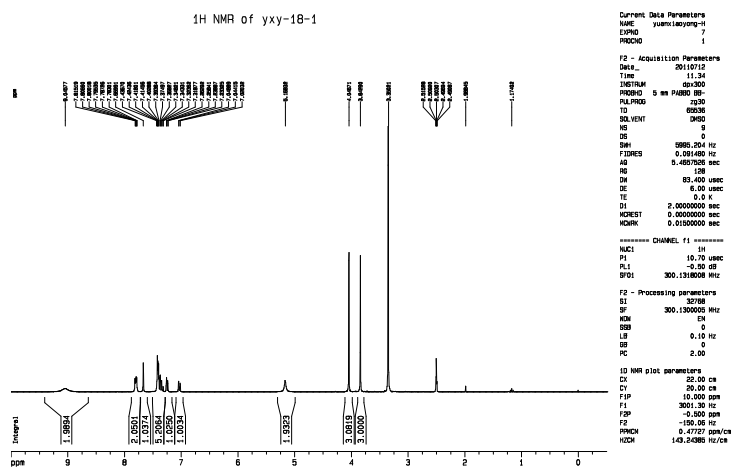


6-08

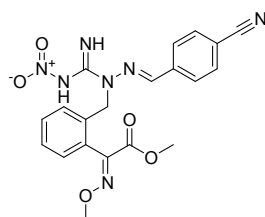


MW 412.1495

¹H NMR of yxy-18-1

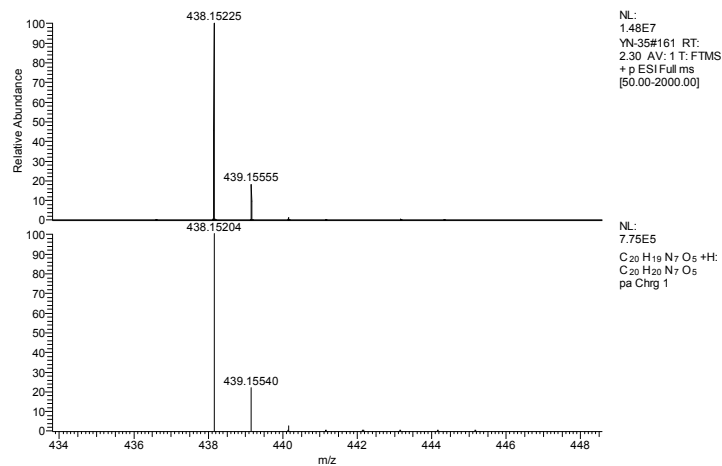
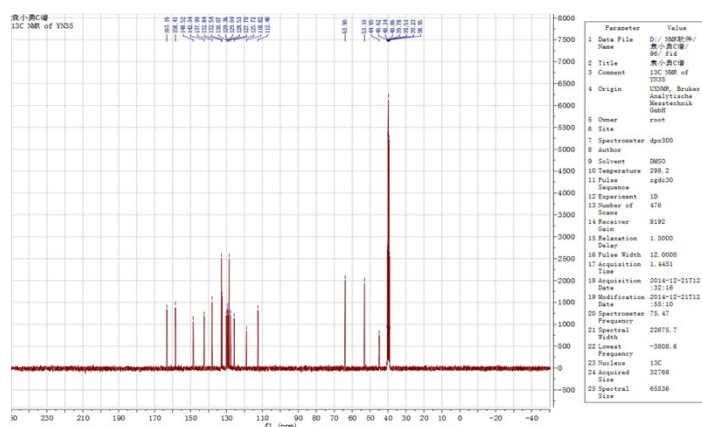
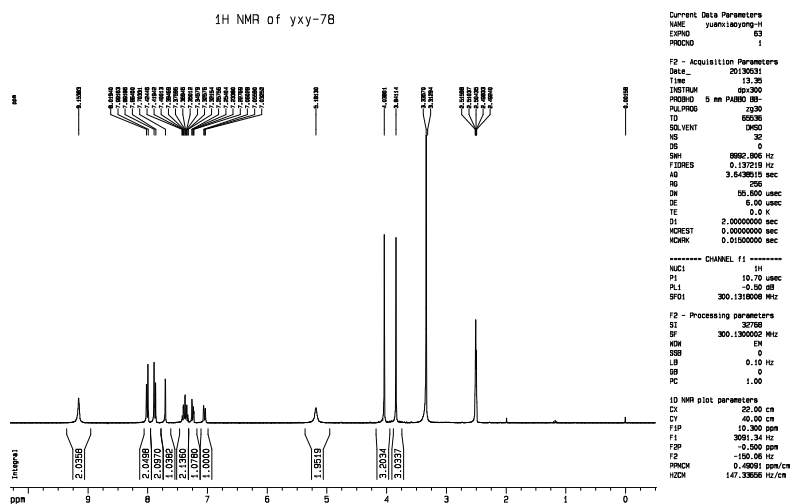


6-09



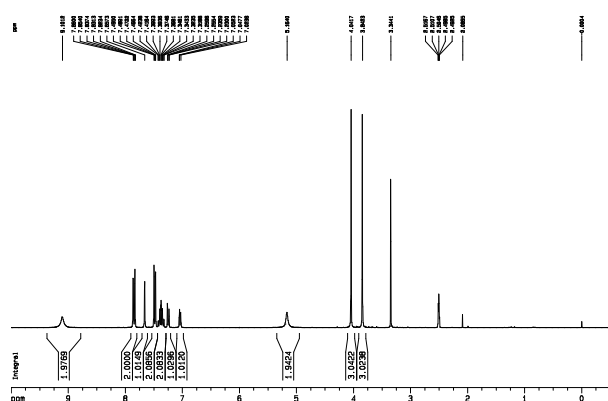
MW 437.1448

¹H NMR of yxy-7B



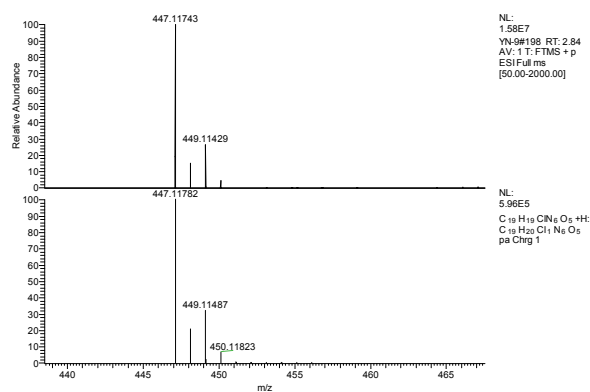
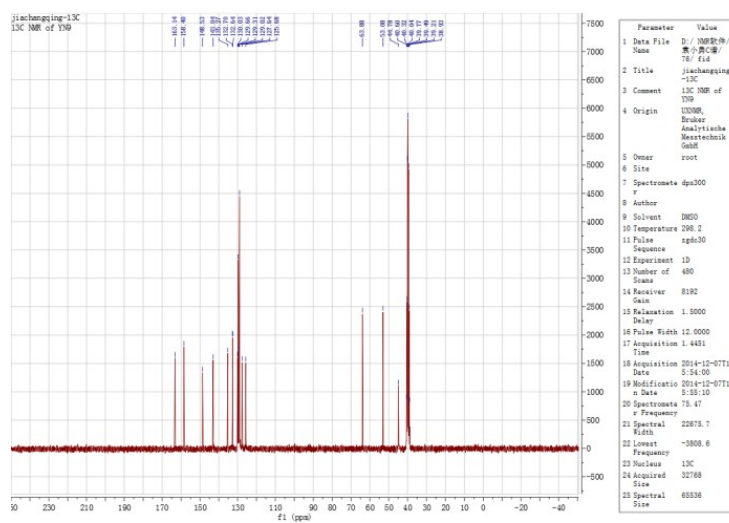
COC(=O)C1=CC=C2C(=C1)N(C(=O)N2[N+](=O)[O-])N=N/C=C/c3ccc(Cl)cc3

1H NMR of 3

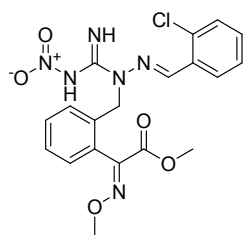


```
Current Data Parameters
Name: yamukajiki-H2
EPOCH: 34
-----
F2 - Acquisition Parameters
Date: 2011/09/03
Time: 13.48
F2 - Acquisition Parameters
P1: 1.000000 sec
P2: 0.000000 sec
P3: 0.000000 sec
P4: 0.000000 sec
P5: 0.000000 sec
P6: 0.000000 sec
P7: 0.000000 sec
P8: 0.000000 sec
P9: 0.000000 sec
P10: 0.000000 sec
P11: 0.000000 sec
P12: 0.000000 sec
P13: 0.000000 sec
P14: 0.000000 sec
P15: 0.000000 sec
P16: 0.000000 sec
P17: 0.000000 sec
P18: 0.000000 sec
P19: 0.000000 sec
P20: 0.000000 sec
P21: 0.000000 sec
P22: 0.000000 sec
P23: 0.000000 sec
P24: 0.000000 sec
P25: 0.000000 sec
P26: 0.000000 sec
P27: 0.000000 sec
P28: 0.000000 sec
P29: 0.000000 sec
P30: 0.000000 sec
P31: 0.000000 sec
P32: 0.000000 sec
P33: 0.000000 sec
P34: 0.000000 sec
P35: 0.000000 sec
P36: 0.000000 sec
P37: 0.000000 sec
P38: 0.000000 sec
P39: 0.000000 sec
P40: 0.000000 sec
P41: 0.000000 sec
P42: 0.000000 sec
P43: 0.000000 sec
P44: 0.000000 sec
P45: 0.000000 sec
P46: 0.000000 sec
P47: 0.000000 sec
P48: 0.000000 sec
P49: 0.000000 sec
P50: 0.000000 sec
P51: 0.000000 sec
P52: 0.000000 sec
P53: 0.000000 sec
P54: 0.000000 sec
P55: 0.000000 sec
P56: 0.000000 sec
P57: 0.000000 sec
P58: 0.000000 sec
P59: 0.000000 sec
P60: 0.000000 sec
P61: 0.000000 sec
P62: 0.000000 sec
P63: 0.000000 sec
P64: 0.000000 sec
P65: 0.000000 sec
P66: 0.000000 sec
P67: 0.000000 sec
P68: 0.000000 sec
P69: 0.000000 sec
P70: 0.000000 sec
P71: 0.000000 sec
P72: 0.000000 sec
P73: 0.000000 sec
P74: 0.000000 sec
P75: 0.000000 sec
P76: 0.000000 sec
P77: 0.000000 sec
P78: 0.000000 sec
P79: 0.000000 sec
P80: 0.000000 sec
P81: 0.000000 sec
P82: 0.000000 sec
P83: 0.000000 sec
P84: 0.000000 sec
P85: 0.000000 sec
P86: 0.000000 sec
P87: 0.000000 sec
P88: 0.000000 sec
P89: 0.000000 sec
P90: 0.000000 sec
P91: 0.000000 sec
P92: 0.000000 sec
P93: 0.000000 sec
P94: 0.000000 sec
P95: 0.000000 sec
P96: 0.000000 sec
P97: 0.000000 sec
P98: 0.000000 sec
P99: 0.000000 sec
P100: 0.000000 sec
P101: 0.000000 sec
P102: 0.000000 sec
P103: 0.000000 sec
P104: 0.000000 sec
P105: 0.000000 sec
P106: 0.000000 sec
P107: 0.000000 sec
P108: 0.000000 sec
P109: 0.000000 sec
P110: 0.000000 sec
P111: 0.000000 sec
P112: 0.000000 sec
P113: 0.000000 sec
P114: 0.000000 sec
P115: 0.000000 sec
P116: 0.000000 sec
P117: 0.000000 sec
P118: 0.000000 sec
P119: 0.000000 sec
P120: 0.000000 sec
P121: 0.000000 sec
P122: 0.000000 sec
P123: 0.000000 sec
P124: 0.000000 sec
P125: 0.000000 sec
P126: 0.000000 sec
P127: 0.000000 sec
P128: 0.000000 sec
P129: 0.000000 sec
P130: 0.000000 sec
P131: 0.000000 sec
P132: 0.000000 sec
P133: 0.000000 sec
P134: 0.000000 sec
P135: 0.000000 sec
P136: 0.000000 sec
P137: 0.000000 sec
P138: 0.000000 sec
P139: 0.000000 sec
P140: 0.000000 sec
P141: 0.000000 sec
P142: 0.000000 sec
P143: 0.000000 sec
P144: 0.000000 sec
P145: 0.000000 sec
P146: 0.000000 sec
P147: 0.000000 sec
P148: 0.000000 sec
P149: 0.000000 sec
P150: 0.000000 sec
P151: 0.000000 sec
P152: 0.000000 sec
P153: 0.000000 sec
P154: 0.000000 sec
P155: 0.000000 sec
P156: 0.000000 sec
P157: 0.000000 sec
P158: 0.000000 sec
P159: 0.000000 sec
P160: 0.000000 sec
P161: 0.000000 sec
P162: 0.000000 sec
P163: 0.000000 sec
P164: 0.000000 sec
P165: 0.000000 sec
P166: 0.000000 sec
P167: 0.000000 sec
P168: 0.000000 sec
P169: 0.000000 sec
P170: 0.000000 sec
P171: 0.000000 sec
P172: 0.000000 sec
P173: 0.000000 sec
P174: 0.000000 sec
P175: 0.000000 sec
P176: 0.000000 sec
P177: 0.000000 sec
P178: 0.000000 sec
P179: 0.000000 sec
P180: 0.000000 sec
P181: 0.000000 sec
P182: 0.000000 sec
P183: 0.000000 sec
P184: 0.000000 sec
P185: 0.000000 sec
P186: 0.000000 sec
P187: 0.000000 sec
P188: 0.000000 sec
P189: 0.000000 sec
P190: 0.000000 sec
P191: 0.000000 sec
P192: 0.000000 sec
P193: 0.000000 sec
P194: 0.000000 sec
P195: 0.000000 sec
P196: 0.000000 sec
P197: 0.000000 sec
P198: 0.000000 sec
P199: 0.000000 sec
P200: 0.000000 sec
P201: 0.000000 sec
P202: 0.000000 sec
P203: 0.000000 sec
P204: 0.000000 sec
P205: 0.000000 sec
P206: 0.000000 sec
P207: 0.000000 sec
P208: 0.000000 sec
P209: 0.000000 sec
P210: 0.000000 sec
P211: 0.000000 sec
P212: 0.000000 sec
P213: 0.000000 sec
P214: 0.000000 sec
P215: 0.000000 sec
P216: 0.000000 sec
P217: 0.000000 sec
P218: 0.000000 sec
P219: 0.000000 sec
P220: 0.000000 sec
P221: 0.000000 sec
P222: 0.000000 sec
P223: 0.000000 sec
P224: 0.000000 sec
P225: 0.000000 sec
P226: 0.000000 sec
P227: 0.000000 sec
P228: 0.000000 sec
P229: 0.000000 sec
P230: 0.000000 sec
P231: 0.000000 sec
P232: 0.000000 sec
P233: 0.000000 sec
P234: 0.000000 sec
P235: 0.000000 sec
P236: 0.000000 sec
P237: 0.000000 sec
P238: 0.000000 sec
P239: 0.000000 sec
P240: 0.000000 sec
P241: 0.000000 sec
P242: 0.000000 sec
P243: 0.000000 sec
P244: 0.000000 sec
P245: 0.000000 sec
P246: 0.000000 sec
P247: 0.000000 sec
P248: 0.000000 sec
P249: 0.000000 sec
P250: 0.000000 sec
P251: 0.000000 sec
P252: 0.000000 sec
P253: 0.000000 sec
P254: 0.000000 sec
P255: 0.000000 sec
P256: 0.000000 sec
P257: 0.000000 sec
P258: 0.000000 sec
P259: 0.000000 sec

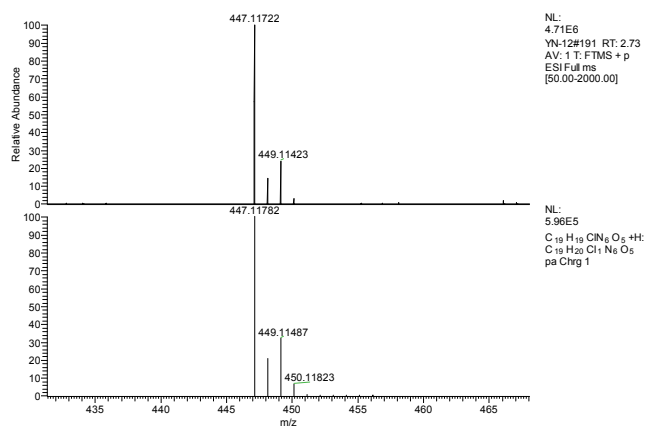
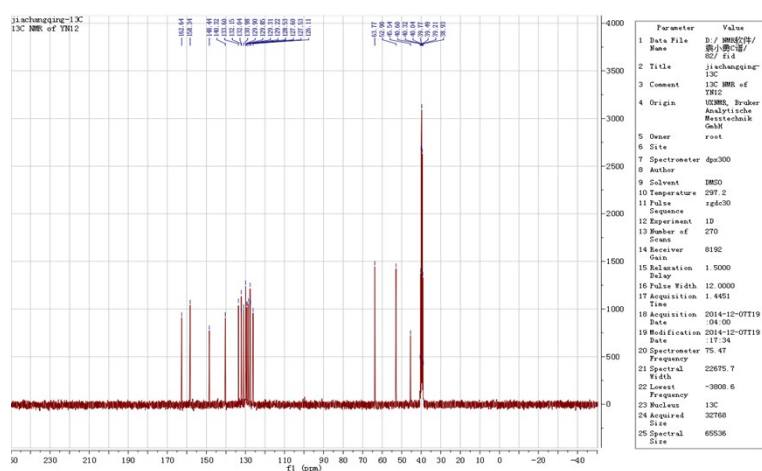
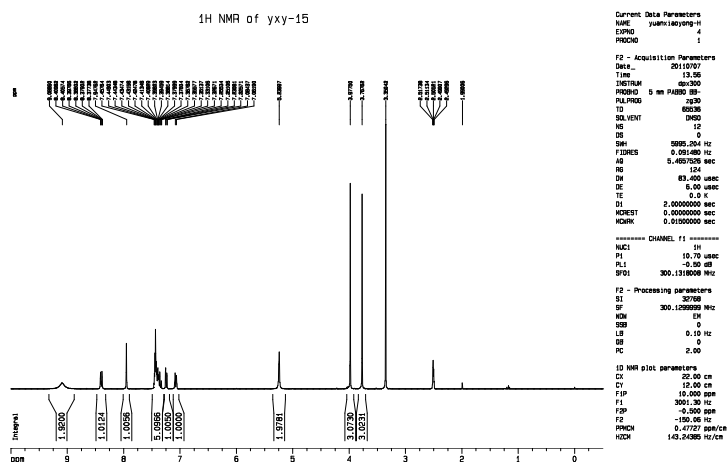
```



6-11

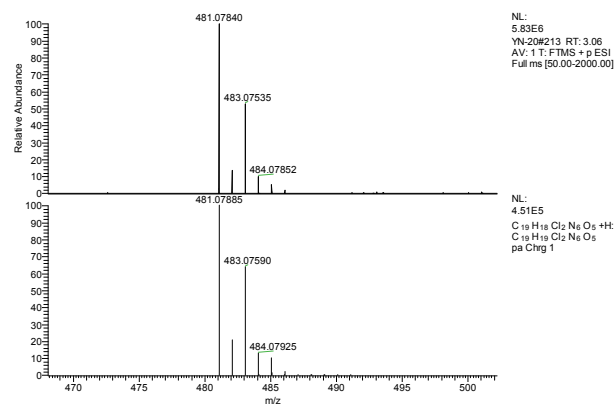
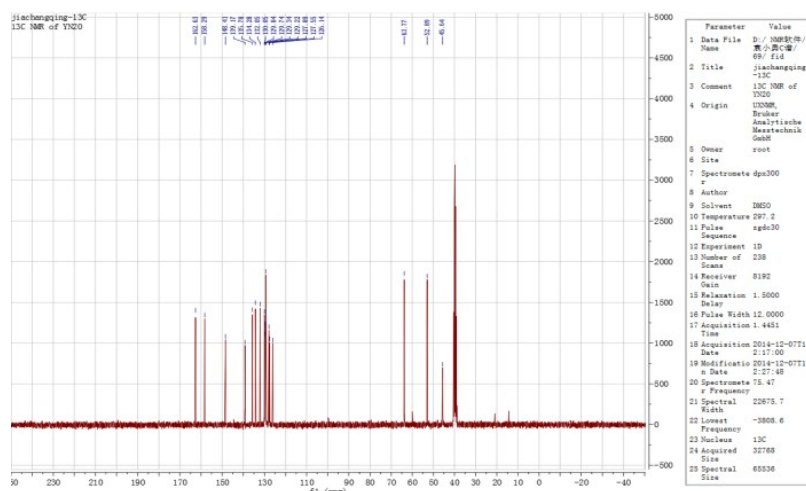
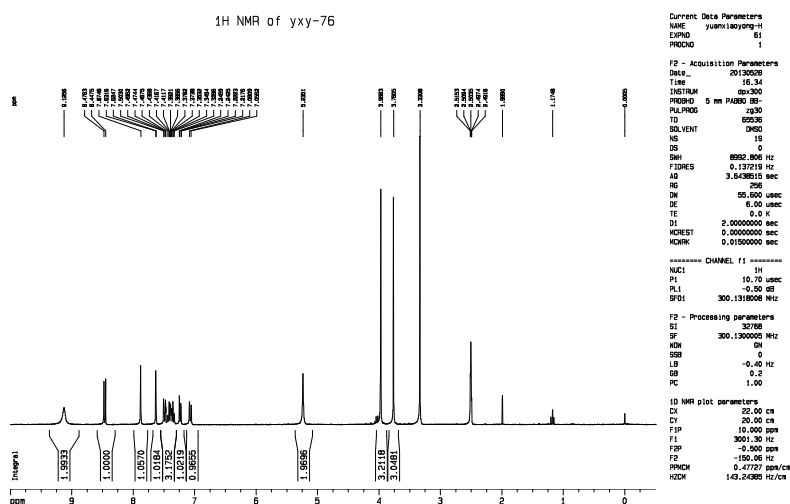


MW 446.1105

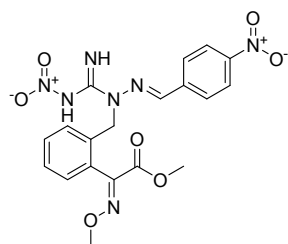


CCOC(=O)C(=O)c1ccccc1Nc2nc(NC(=O)c3ccc(Cl)cc3Cl)c(=O)[N+](=O)[O-]

¹H NMR of yxy-76

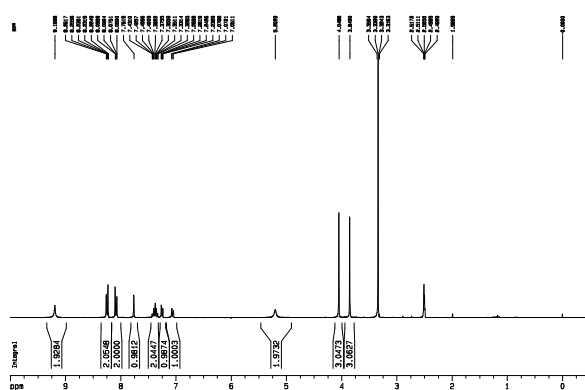


6-13



MW 457.1346

¹H NMR of yxy-21



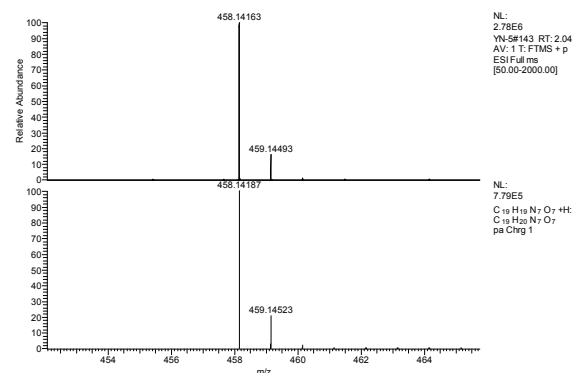
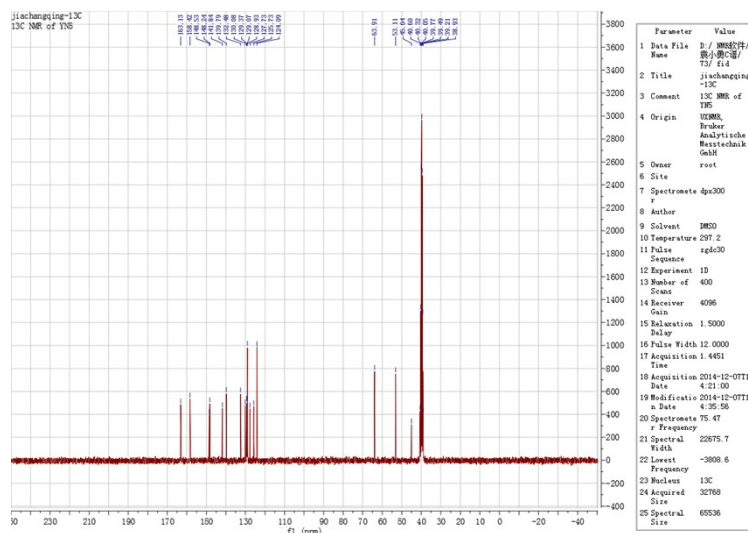
Current Data Parameters
NAME yxy-21
EXPNO 8
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110722
Time 15.25
INSTRUM spect
PROBHD 5 mm PABBO 90-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 7
DS 0
SWH 8998.264 Hz
FIDRES 0.091480 Hz
AQ 0.4807550 sec
RG 156
GB 0
PC 60.000 usec
DE 6.24 usec
TE 298.2 K
D1 2.00000000 sec
ACQST 0.00000000 sec
PCPRG 0.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 10.70 usec
PL1 -0.50 dB
SFO1 300.1310000 MHz

F2 - Processing parameters
SI 32768
SF 300.1310000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 2.00

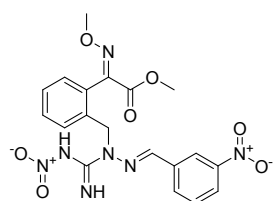
1D NMR plot parameters
CX 60.00 cm
CY 12.00 cm
FID 10.000 mm
PI 3601.20 Hz
F2 -0.000 mm
F2 -180.00 Hz
PCPRG 0.4777 sec/sec
PCPRG 143.24000 Hz/sec



NL:
2.78E6
YN-58143 RT: 2.04
AV-1 T: FTMS + p
ESI(Full.ms
[50.00-2000.00])

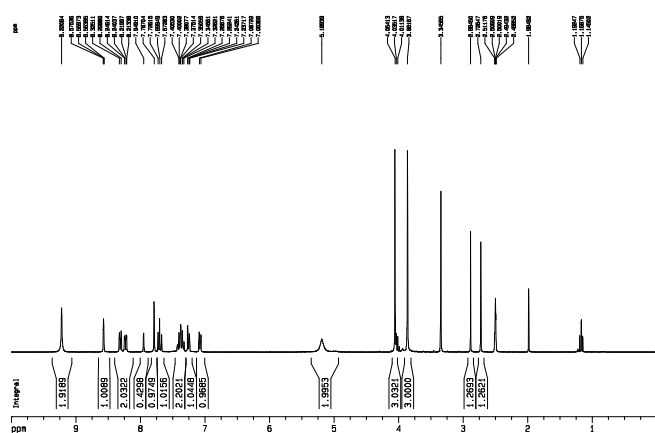
NL:
7.79E5
C19H19N7O7 +H:
C19H20N7O7
pa Chrg 1

6-14



MW 457.1346

¹H NMR of yxy-26



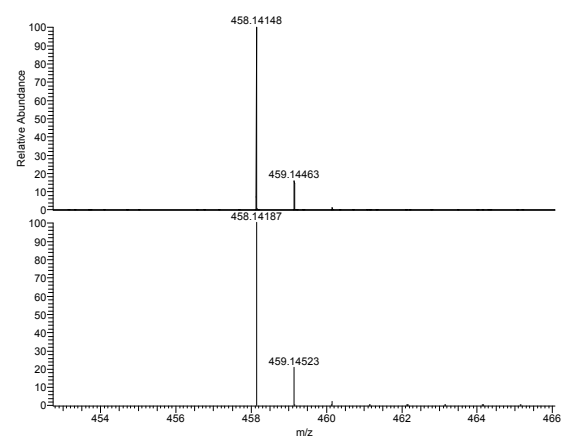
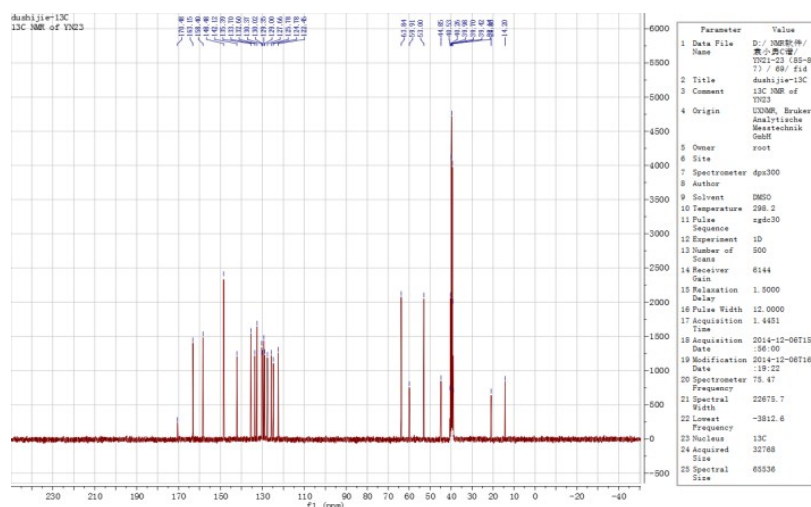
Current Data Parameters
NAME yxy-26
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130407
Time 14.42
INSTRUM spect
PROBHD 5 mm PABBO 5B-
PULPROG zgpg30
TD 65536
SOLVENT DMSO
DS 0
SS 0
SM 655.806 Hz
FIDRES 0.137016 Hz
AQ 3.6438515 sec
RG 124
DM 55.600 usec
DE 6.00 usec
TE 300.2 K
D1 2.0000000 sec
HDCST 0.0000000 sec
HXRK 0.0150000 sec

----- CHANNEL f1 -----
NUC1 1H
P1 10.70 usec
PL1 -0.00 dB
SFO1 300.1310000 MHz

F2 - Processing parameters
SI 32768
SF 300.1300013 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

ID NMR plot parameters
CX 25.00 cm
CY 7.00 cm
FIP 10.000 ppm
FI 3001.30 Hz
FSP 0.000 ppm
FZ 0.00 Hz
PRNH 0.45450 ppm/c
HZCN 136.42273 Hz/cm

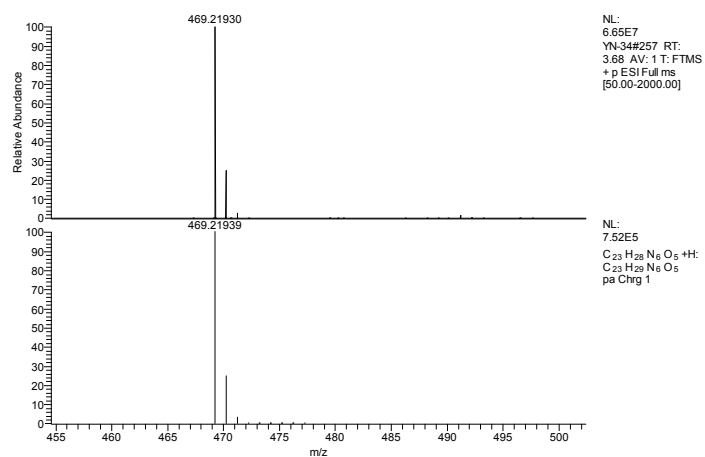
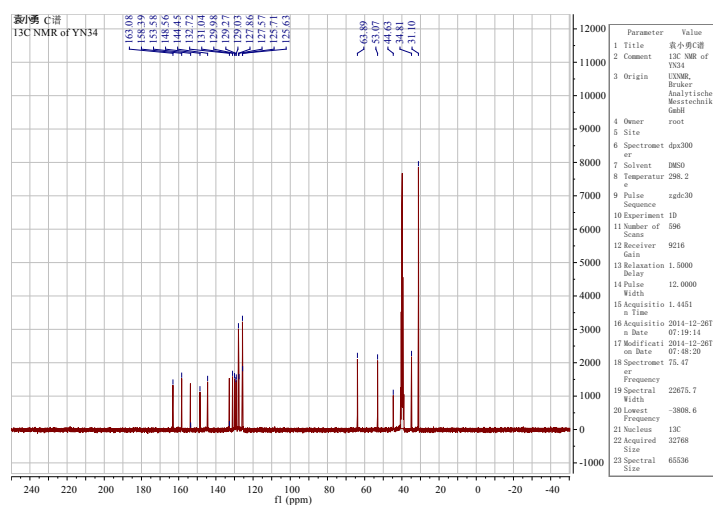
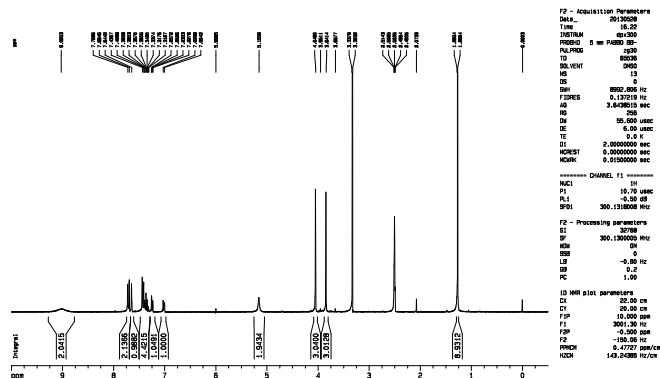


NL:
4.33E6
YN-23#152-177
RT: 2.18-2.54 AV:
26 T: FTMS + p ESI
Full ms
[50.00-2000.00]

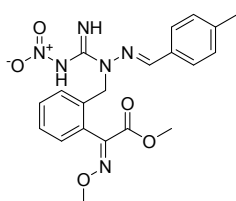
NL:
7.79E5
C 19 H 19 N 7 O 7 +H
C 19 H 20 N 7 O 7
pa Chrg 1

CCOC(=O)C1=CC=C2C(=C1)C(=N2)C(=N1)C(=O)N1C(=O)N1[N+](=O)[O-]

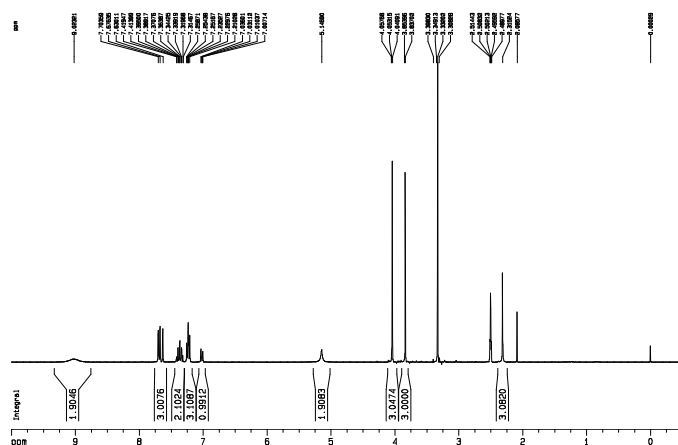
¹H NMR of γxy-77



6-16



MW 426.1652

¹H NMR of 4

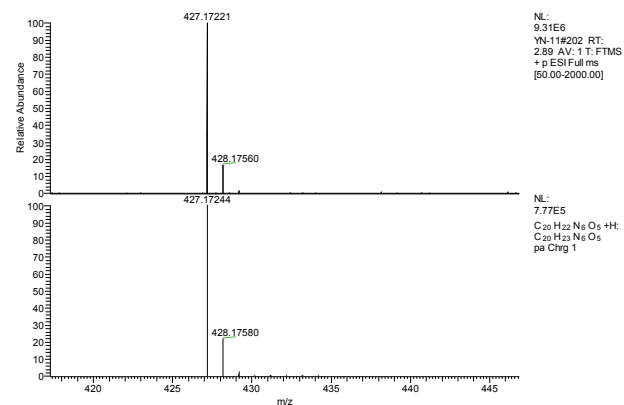
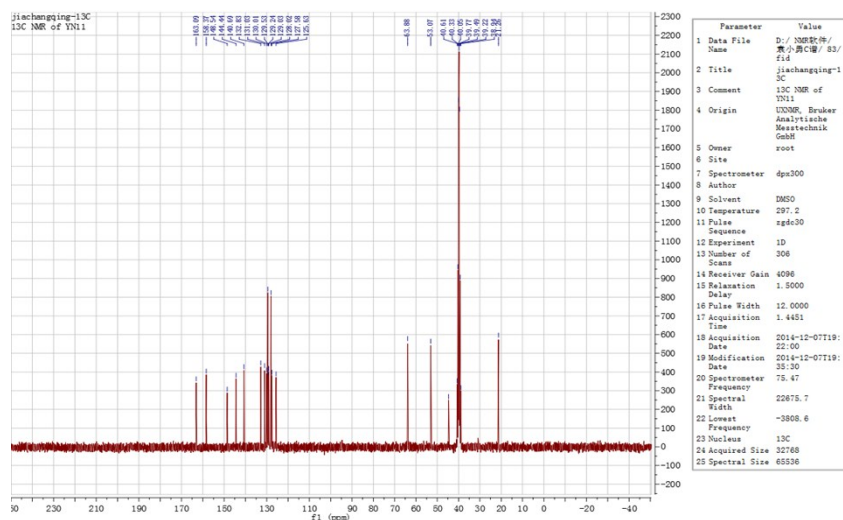
Current Data Parameters
NAME yuanyuanyong-H
EXPNO 33
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110603
Time 13.56
INSTRUM gpc300
PROBHD 5 mm PA880 B8-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 6
DS 0
SWH 19995.204 Hz
FIDRES 0.091480 Hz
AQ 5.4657256 sec
RG 256
DN 83.400 usec
DE 6.00 usec
TE 298.2 K
D1 2.0000000 sec
NOREST 0.0000000 sec
NMRK 0.0150000 sec

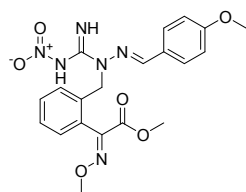
===== CHANNEL f1 =====
NUC1 1H
P1 10.70 usec
PL1 -0.50 dB
SFO1 300.1318008 MHz

F2 - Processing parameters
SI 32768
SF 300.1300008 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 29.00 cm
CY 12.00 cm
F1P 16.000 ppm
F1 3001.30 Hz
F2P -10.000 ppm
F2 -106.06 Hz
PRNCH 0.4727 ppm/cm
H2CH 143.24880 Hz/cm

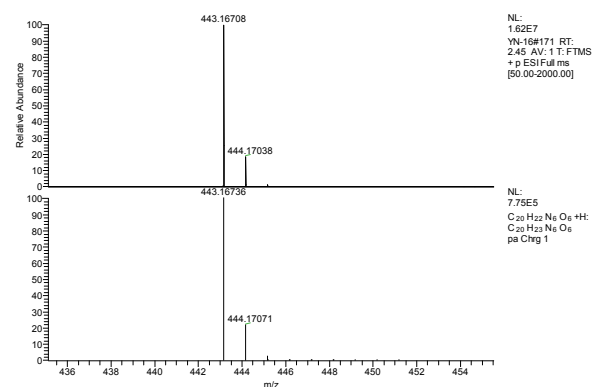
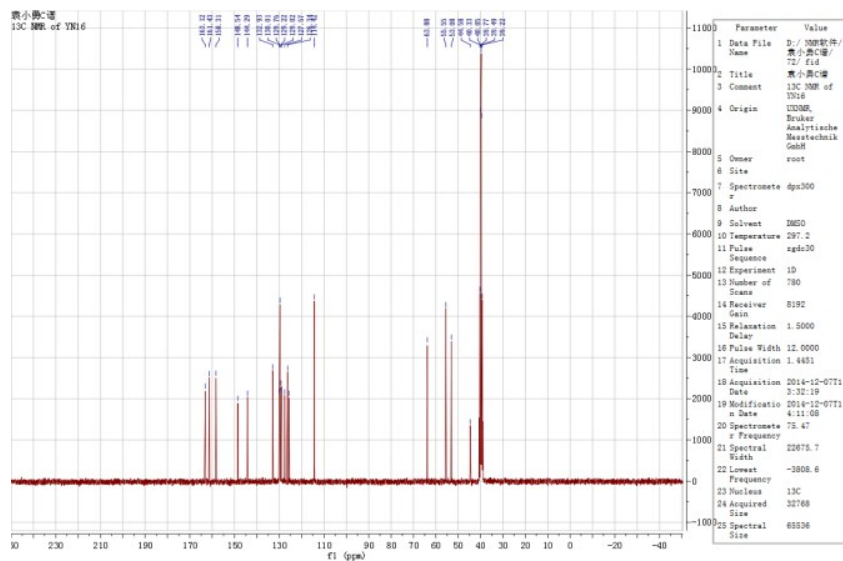
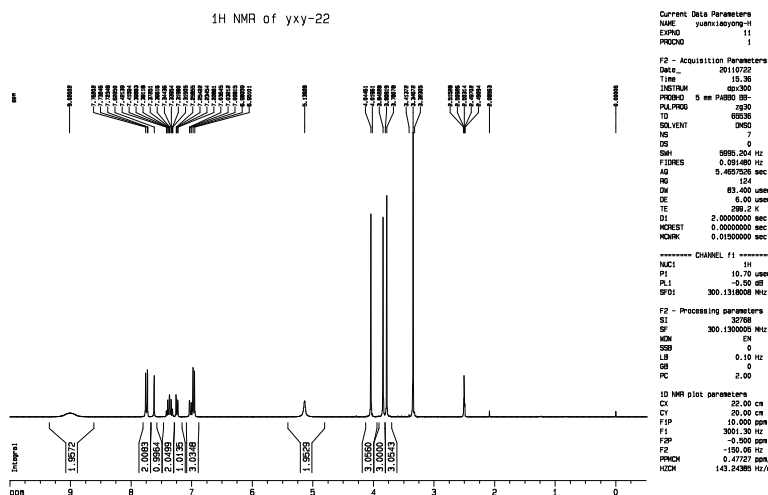


6-17



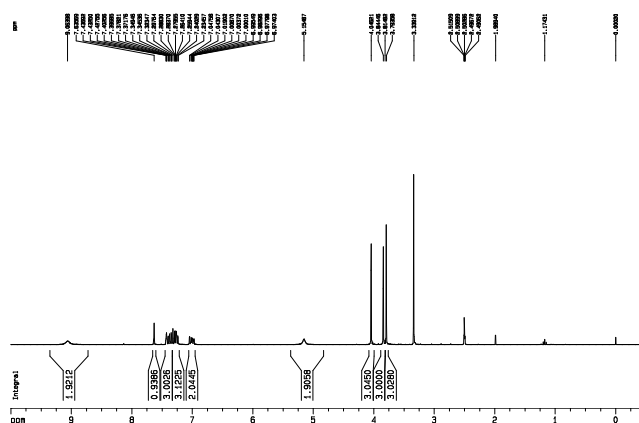
MW 442.1601

¹H NMR of yxy-22



COC(=O)C(=O)c1ccccc1Nc2nc([N+](=O)[O-])cnc2N=Cc3ccc(OC)cc3

¹H NMR of yxy-1



```

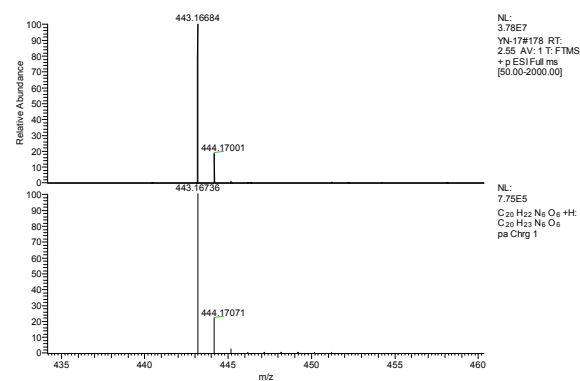
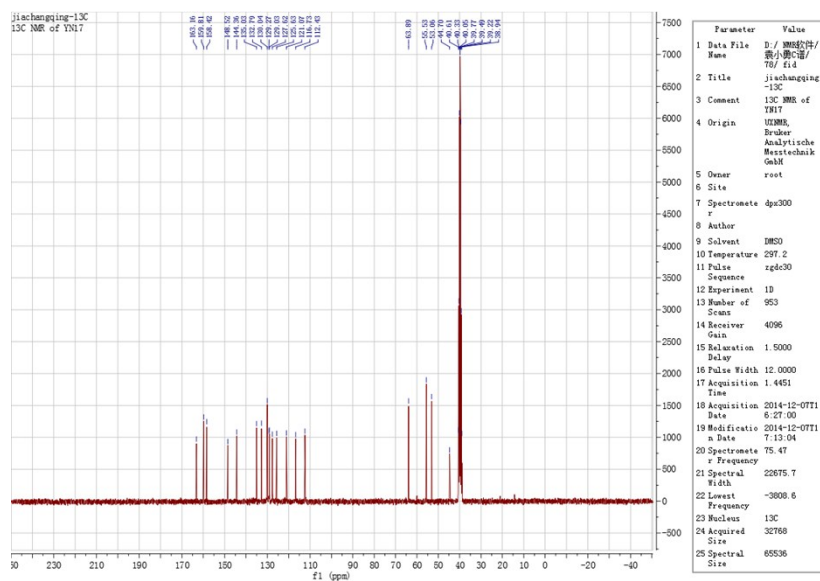
Current Data Parameters
NAME      yuanshu1941
UNIT      36
MODE      1
PRECED    1

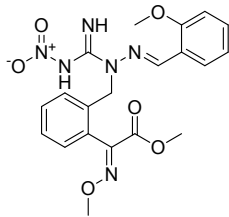
F2 - Acquisition Parameters
Date..... 20110815
Time..... 11:14
INSTRUM   mp300
PROBID    50 PABBO 180
FIDRES    5.467000 Hz
RG         128
SOLVENT    DMSO
NS         6
DS         2
SWH         5999.204 MHz
F2RES     0.091480 Hz
AQ         5.467000 sec
RG         128
DE         6.00 K
F2HRES    0.0912 K
ACQRES    2.00000000 sec
MCHRES    0.00000000 sec
MCHRES    0.01300000 Hz
===== CHANNEL f1 =====
NUC1      1H
NUC1F     10.70 usec
GB         0
SFO1      300.1310080 MHz

F2 - Processing parameters
SI         30768
SF         300.1310080 MHz
WDW         EM
SSB         0
LB         0.10
PC         2.00

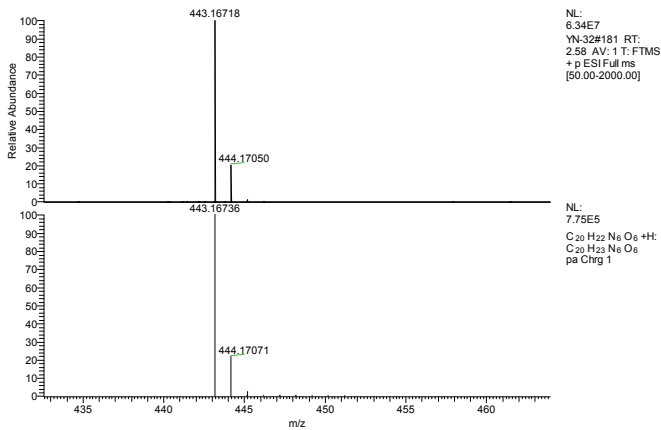
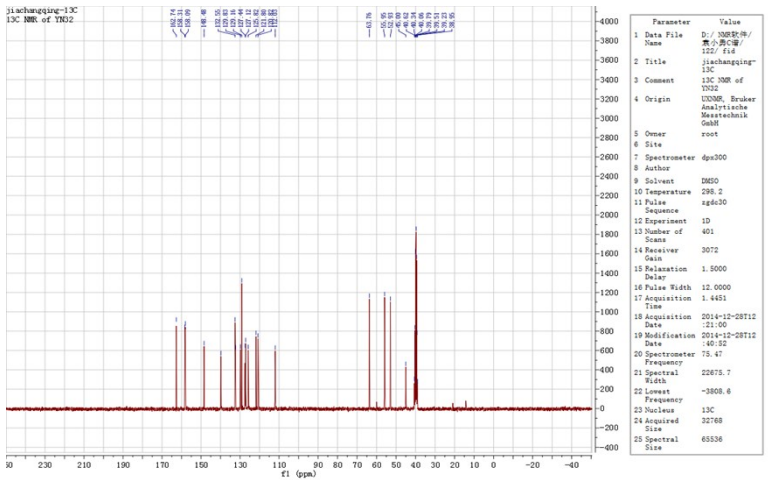
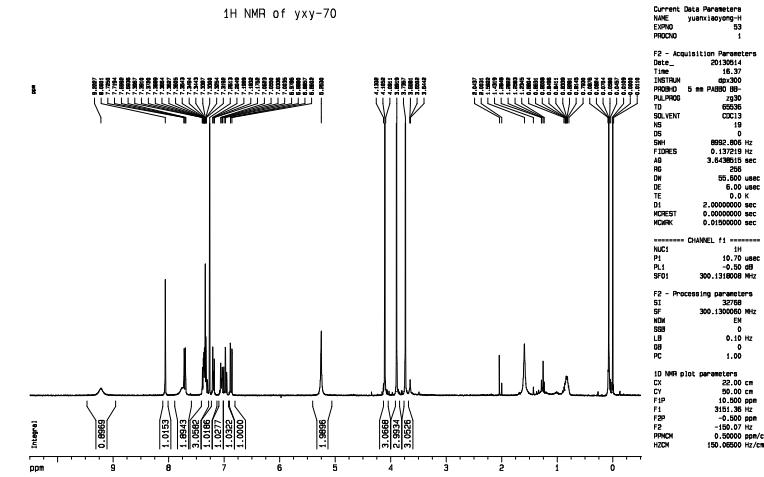
ID WHR plot parameters
CX         25.00 cm
CY         6.00 cm
F1         10.000 ppm
F2         300.130 ppm
F3         10.000 ppm
F4         -1.906 Hz
F5         0.000 ppm/cx
H2H2       143.248 MHz/cx

```



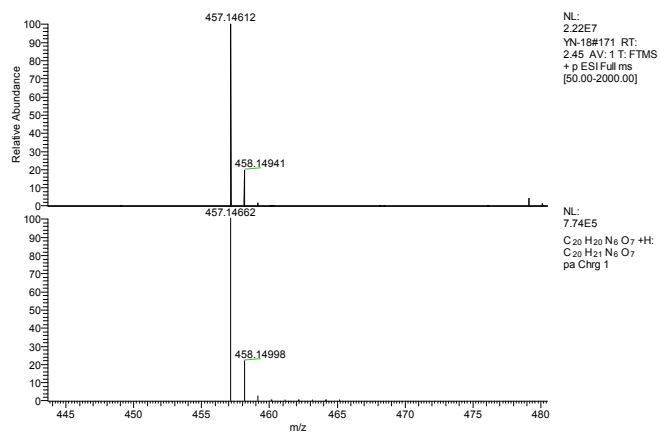
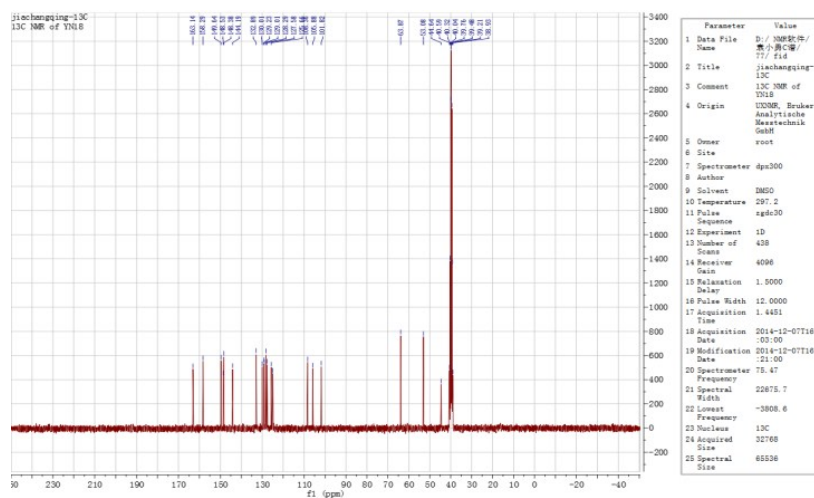
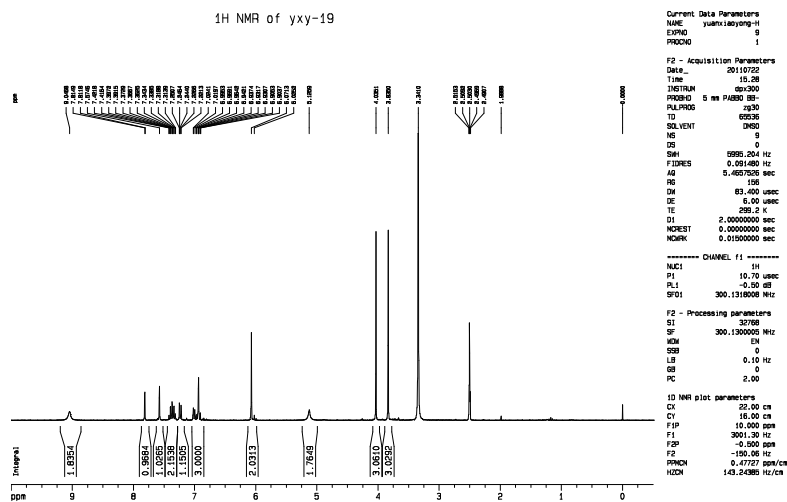


MW 442.1601



COC(=O)C(=O)c1ccccc1CN(C(=O)O[N+](=O)[O-])N=Cc2ccc3c(c2)OCO3

¹H NMR of vxv-19



COC(=O)c1c2ccccc2c(c1)C(=N1C(=O)N1[N+](=O)[O-])N=N/C=C/c3cc(OC4=CC=CC=C4)ccc3 MW 504.1757

¹H NMR spectrum (CDCl₃) of compound 1. The spectrum shows peaks at 9.13 (s, 1H), 7.13-7.10 (m, 4H), 6.92 (s, 1H), 5.00 (s, 1H), 3.07 (s, 3H), and 3.00 (s, 3H). Integration values are shown below the peaks. An inset shows the ¹³C NMR spectrum with peaks from 155.1 to 15.2 ppm.

```

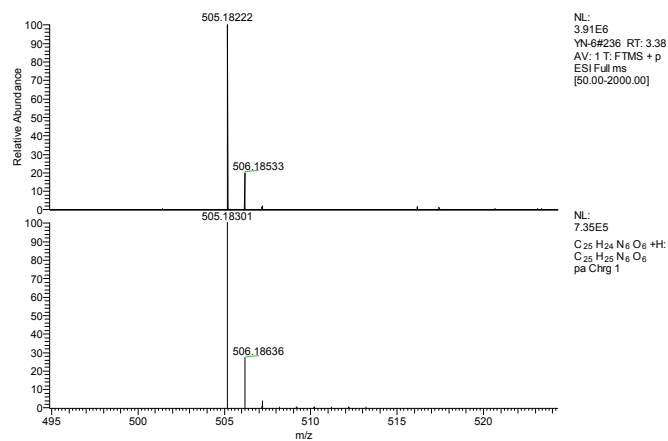
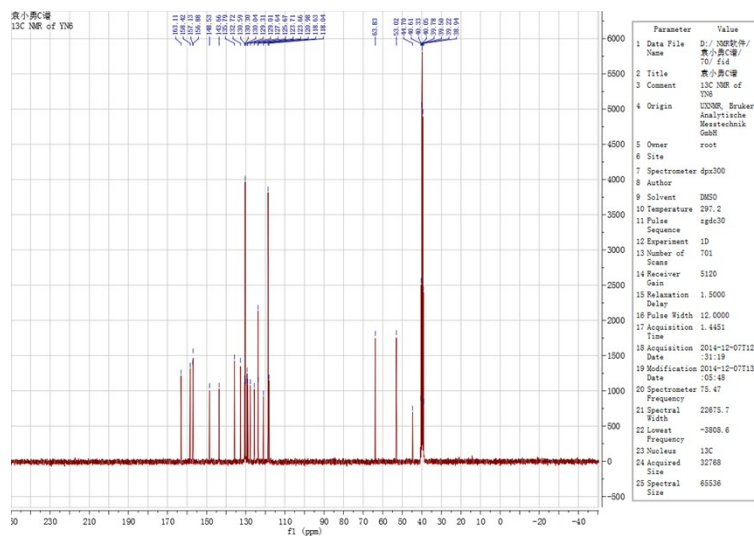
Current Data Parameters
Name:       pwna1cayp-h-0
EXPNO      0
PROCNO     0
PROCGR     0
NAME       pwna1cayp-h-0
PULPROG    sm
SOLVENT     DMSO
NS          0
DS          0
SWH          5069.250 Hz
AQ          0.10000000 Hz
RG          124
DE          5.00 uArc
RG          0.8 x
PC          1.20000000 sec
HDCREST     0.00000000 sec
HDCRST      0.00000000 sec
HDCRST      0.00000000 sec

===== CHANNEL 1 =====
PL1         -10.70 dB
PL2         -10.70 dB
PL3         -10.70 dB
SFO          300.1310000 MHz

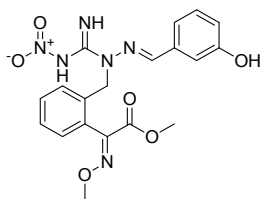
F2 - Processing parameters
SI           30768
SF           300.1310000 MHz
WDW          EM
SSB          0
GB           0.10 Hz
PC           2.00 Hz
LB           2.00 Hz

10 NMR plot parameters
SI           32.00 cm
SF           18.00 MHz
F1           15.00 ppm
F2           3600.10 Hz
WDW          EM
SSB          0
GB           0.10 Hz
PC           2.00 Hz
LB           2.00 Hz
FWDCH        8.4727 MHz
FWDCH        143.4000 MHz

```

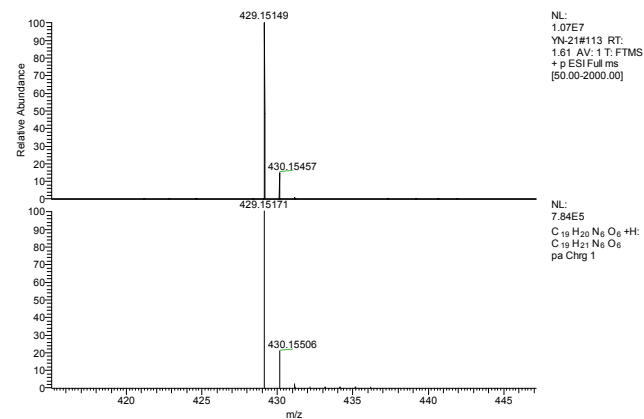
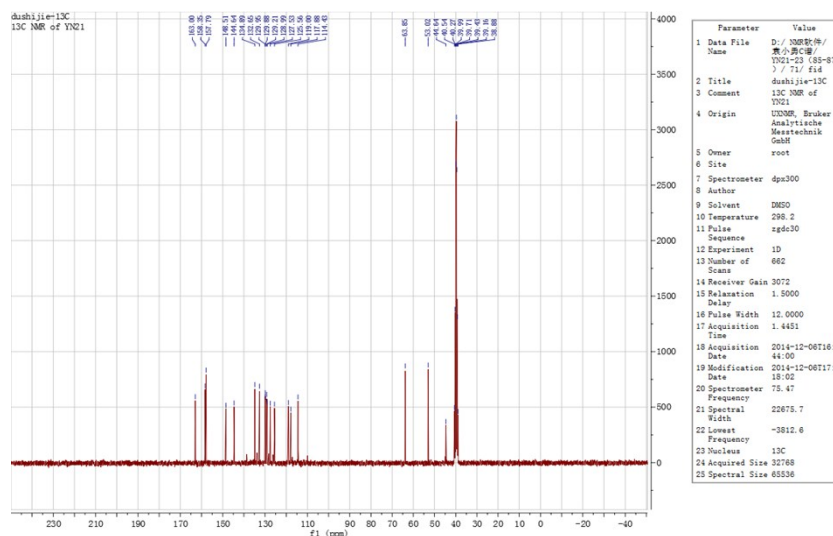
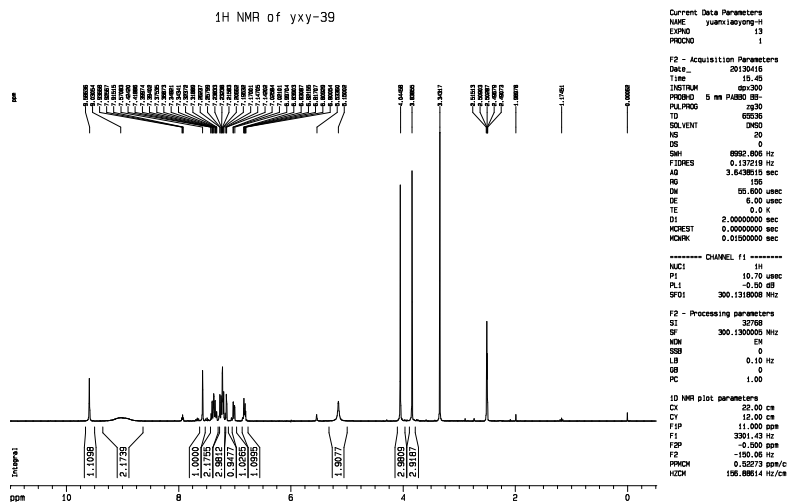


6-22

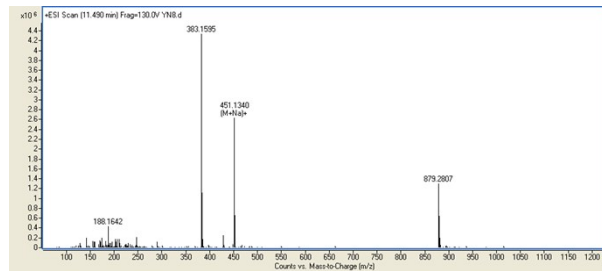
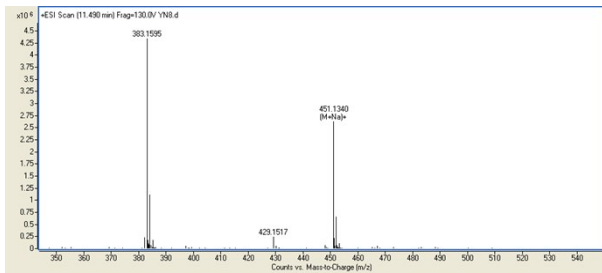
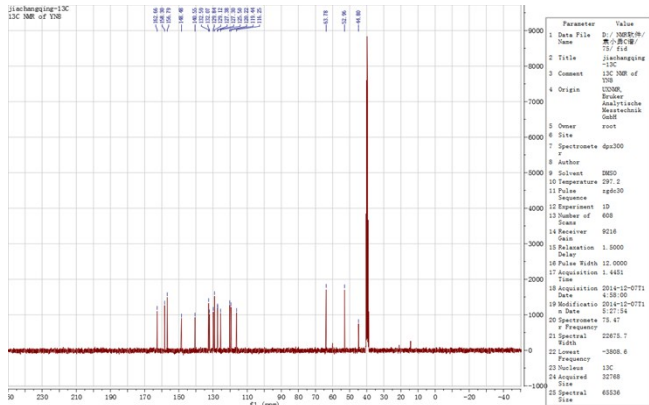
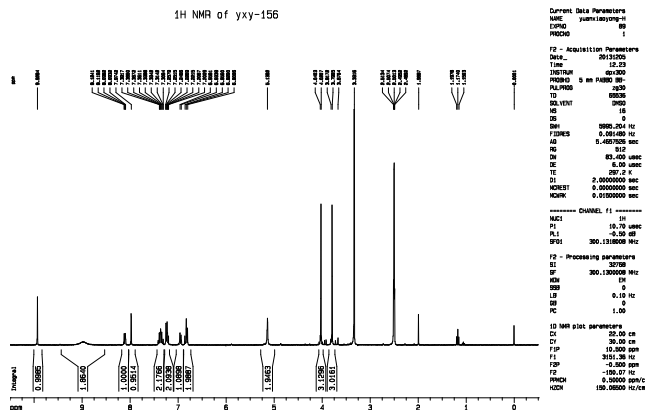
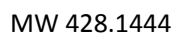


MW 428.1444

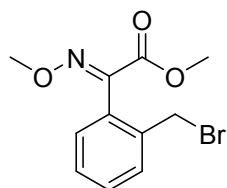
¹H NMR of yxy-39



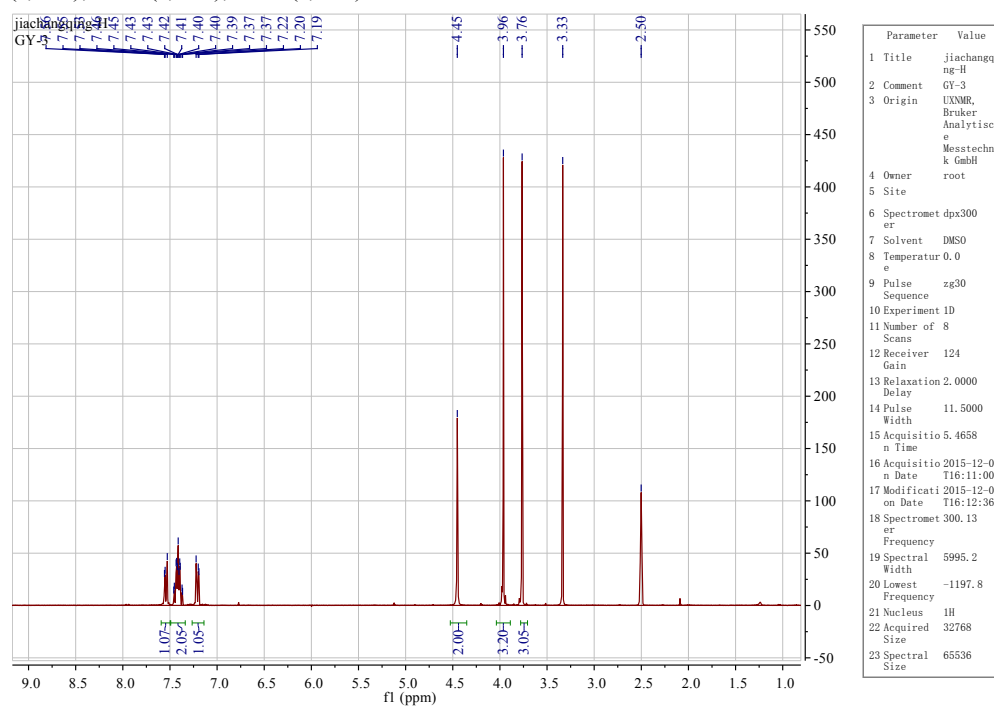
6-23



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



^1H NMR (300 MHz, $\text{DMSO}-d_6$) 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).



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

^1H NMR (600 MHz, CDCl_3): 3.86 (3H, s, $-\text{COOMe}$), 4.04 (3H, s, $\text{N}-\text{OCH}_3$), 4.31 (2H, s, $-\text{CH}_2-$), 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).