Electronic supplementary materials *Mendeleev Commun.*, 2016, **26**, 220−222

Convenient synthesis of α-dichloromethylpyridines from 3-trichloromethyl-1,2,4-triazines

Nikolay V. Chepchugov, Dmitry S. Kopchuk, Igor S. Kovalev, Grigory V. Zyryanov, Vladimir L. Rusinov and Oleg N. Chupakhin

General

All common reagents and solvents were used as purchased. Melting points were measured on the instrument Boetius. NMR spectra were acquired on a Bruker Avance-400 spectrometer, 298 K, digital resolution ± 0.01 ppm, using TMS as internal standard. Mass-spectra were recorded on MicrOTOF-Q II (Bruker Daltonics), electrospray as a method of ionization. Microanalyzes (C, H, N) were performed using a Perkin–Elmer 2400 elemental analyzer.

Synthesis

Trizines **1a,c** were synthesized as described in literature[1].

6-(4-Methoxyphenyl)-3-trichloromethyl-1,2,4-triazine (1b). Synthesis was carried out in accordance with the literature method for similar compounds.[1] Yield 70%. Mp 142-144 °C. ^{1}H NMR, δ, ppm ($CDCl_3$, *J*, Hz): 3.92 (3H, s, MeO), 7.11 (2H, m, 4-$MeOC_6H_4$), 8.17 (2H, m, 4-$MeOC_6H_4$), 9.10 (1H, s, H-5). **ESI-MS**, *m/z*: found 303.98, required 303.98 $(M+H)^+$. Calc. for $C_{11}H_8Cl_3ON_3$ (%): C 43.38; H 2.65; N 13.80. Found (%): C 43.21; H 2.53; N 13.59.

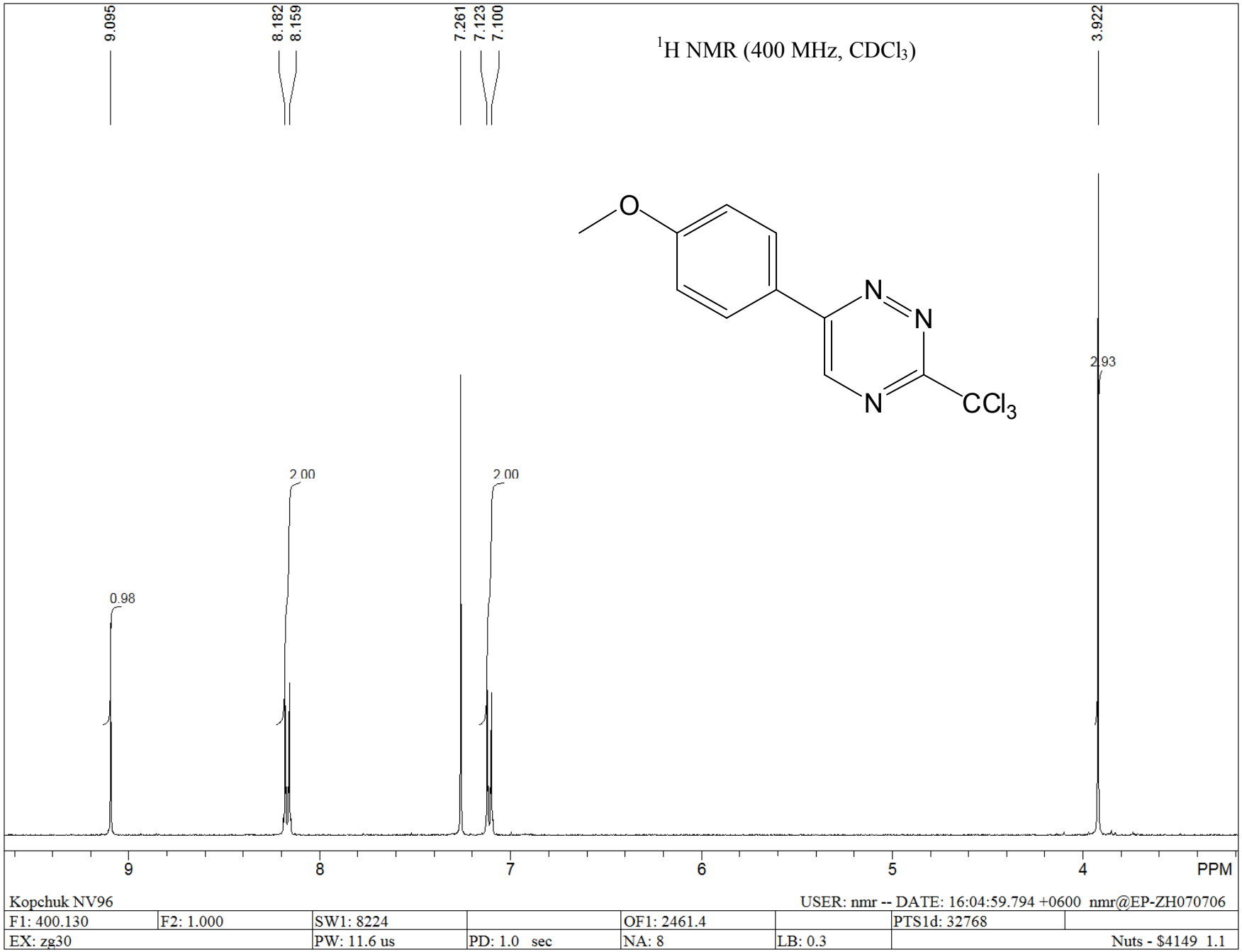
1-Dichloromethyl-4-(4-methoxyphenyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine (3b). Yield 210 mg (0.75 mmol, 75%). Mp 104-106 °C. ^{1}H NMR, δ, ppm ($CDCl_3$, *J*, Hz): 2.15 (2H, m, CH_2-6), 3.00 (2H, t, *J* = 7.6, CH_2-7), 3.26 (2H, t, *J* = 7.6, CH_2-5), 3.85 (3H, s, MeO), 6.83 (1H, s, $CHCl_2$), 6.99 (2H, m, 4-$MeOC_6H_4$), 7.37 (2H, m, 4-$MeOC_6H_4$), 8.36 (1H, s, H-3). ^{13}C NMR, δ, ppm ($CDCl_3$): 25.2, 30.6, 32.5, 55.4 (MeO), 71.4 ($CHCl_2$), 114.2, 129.4, 129.7, 135.0,

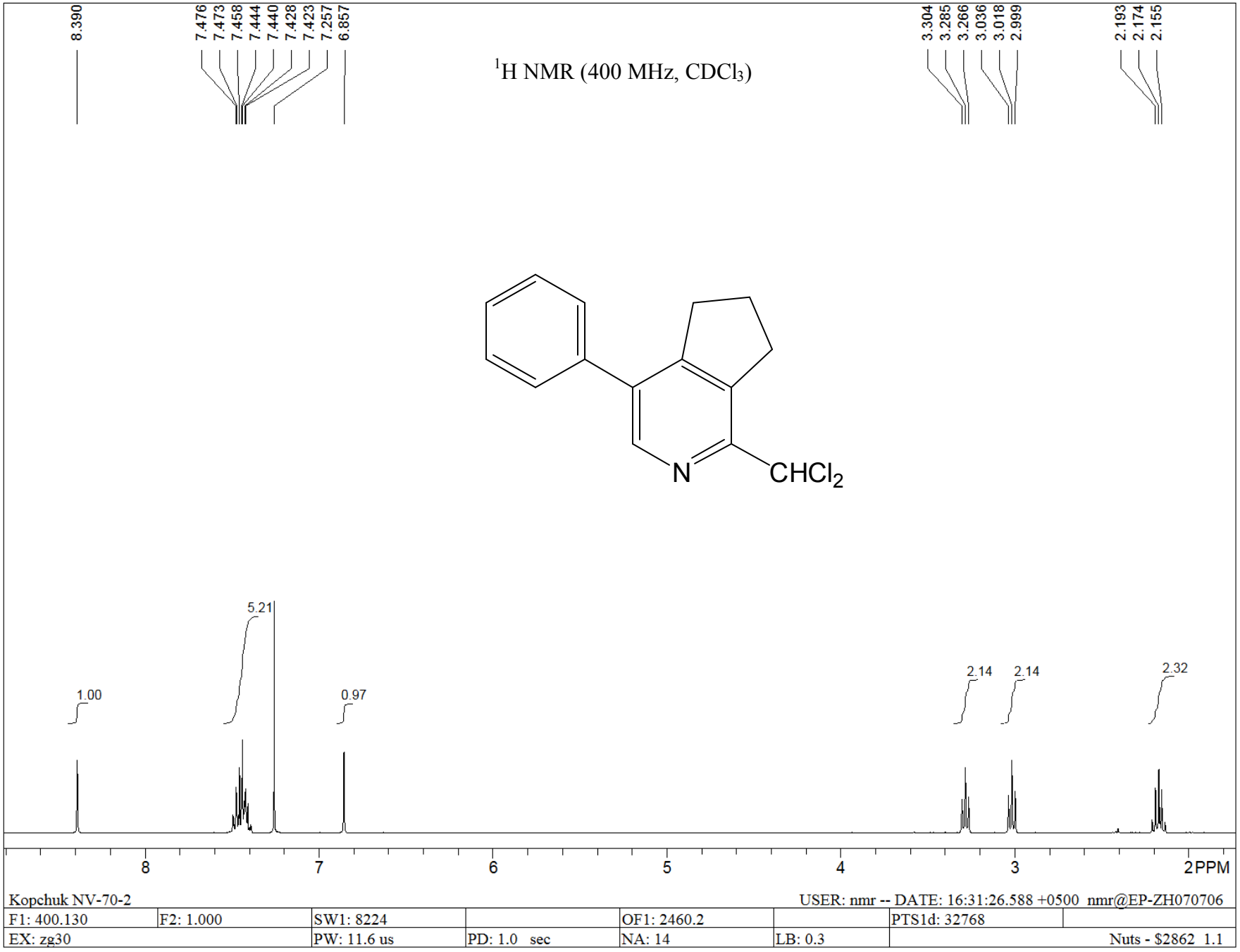
137.7, 146.1, 150.2, 153.7, 159.6. **ESI-MS**, *m/z*: found 308.06, required 308.06 $(M+H)^+$. Calc. for $C_{16}H_{15}Cl_2ON$ (%): C 62.35; H 4.91; N 4.54. Found (%): C 62.19; H 4.77; N 4.42.

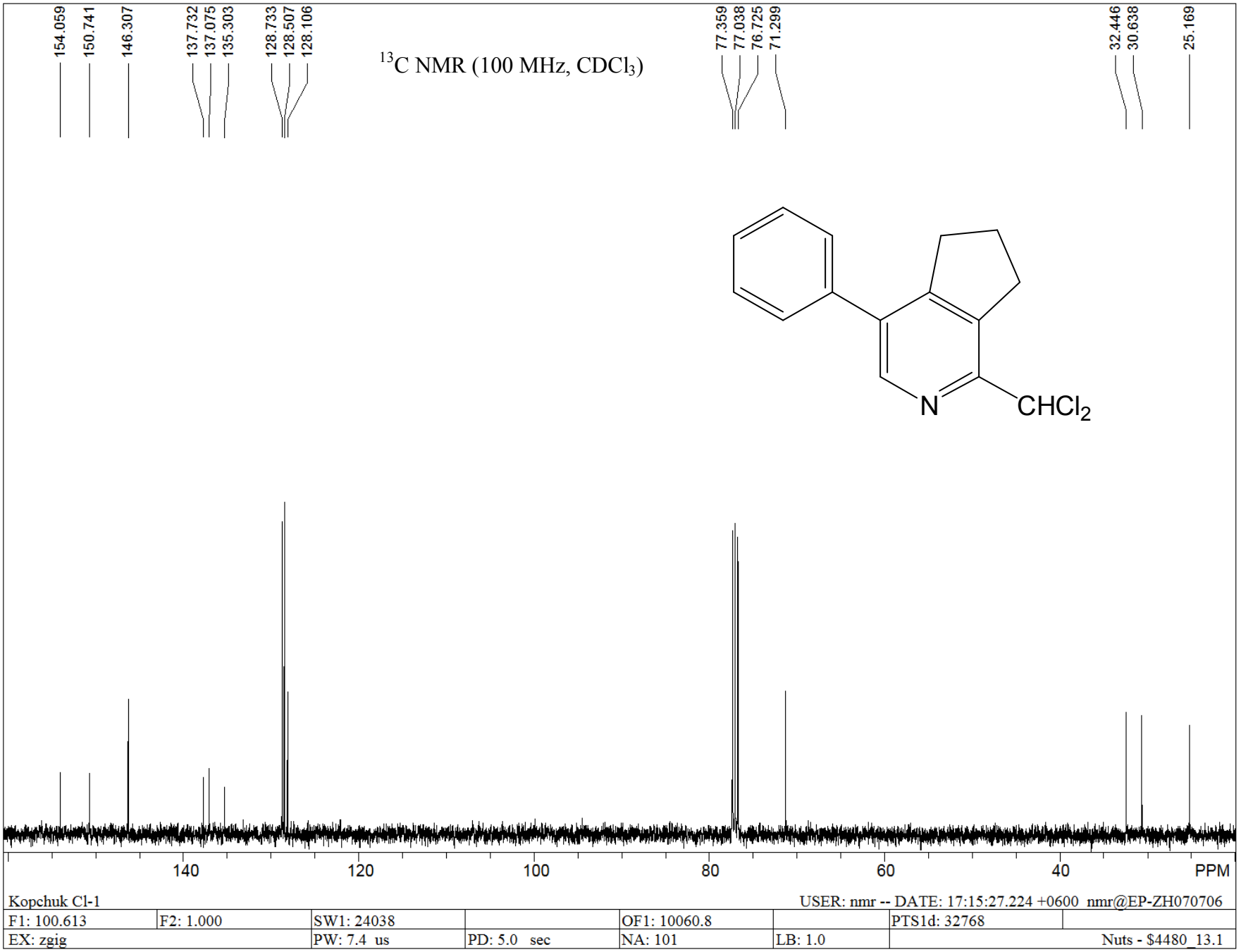
4-(4-Chlorophenyl)-1-dichloromethyl-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine (3c). Yield 240 mg (0.77 mmol, 77%). Mp 109-111 °C. ^{1}H NMR, δ, ppm ($CDCl_3$, *J*, Hz): 2.11 (2H, m, CH_2-6), 2.91 (2H, t, *J* = 7.6, CH_2-7), 3.21 (2H, t, *J* = 7.6, CH_2-5), 6.76 (1H, s, $CHCl_2$), 7.29 (2H, m, 4-ClC_6H_4), 7.38 (2H, m, 4-ClC_6H_4), 8.28 (1H, s, H-3). ^{13}C NMR, δ, ppm ($CDCl_3$): 24.1, 29.6, 31.4, 70.2 ($CHCl_2$), 128.0, 128.8, 133.1, 133.3, 134.5, 136.9, 145.1, 150.1, 153.0. **ESI-MS**, *m/z*: found 312.01, required 312.01 $(M+H)^+$. Calc. for $C_{15}H_{12}Cl_3N$ (%): C 57.63; H 3.87; N 4.48. Found (%): C 57.40; H 3.71; N 4.32.

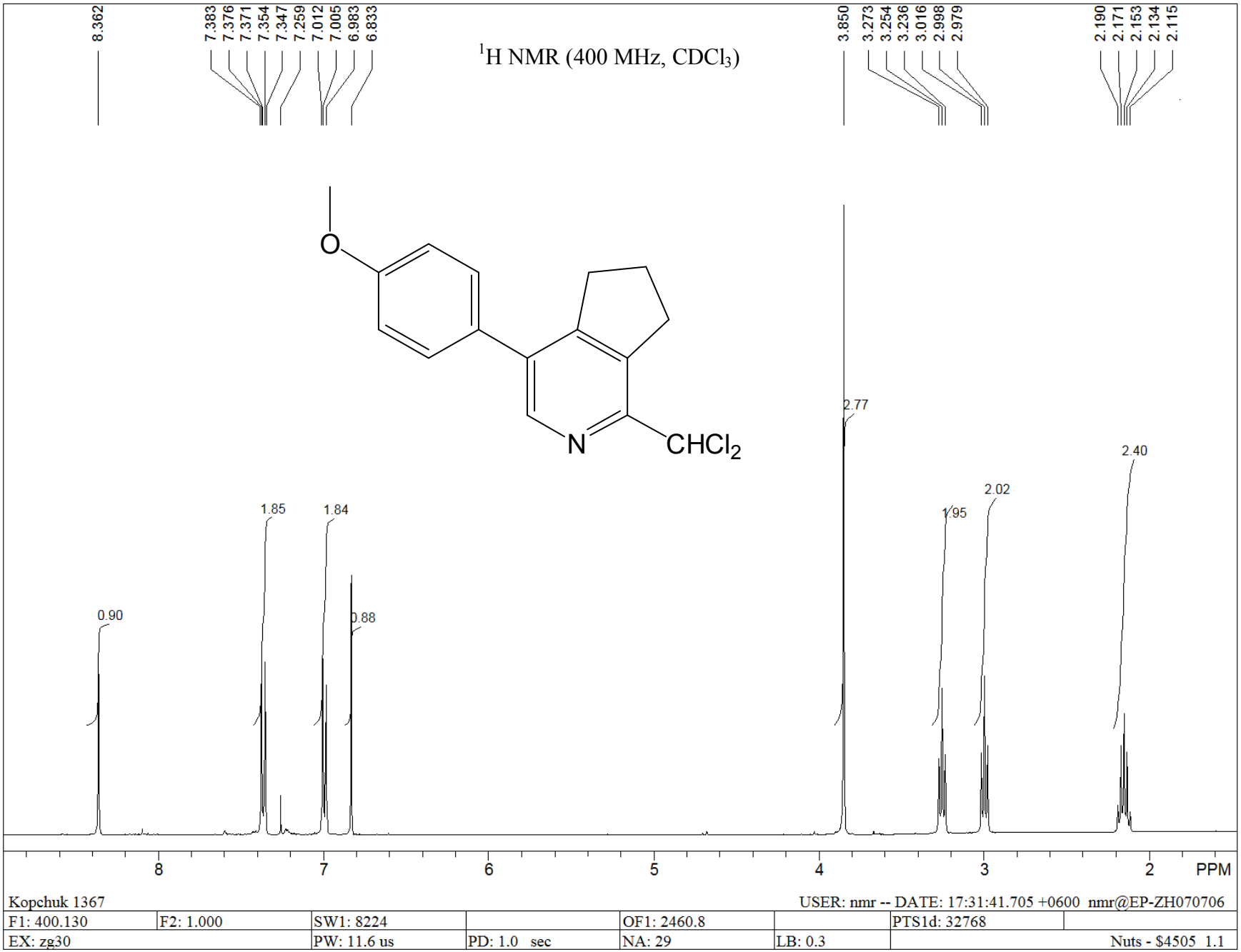
References

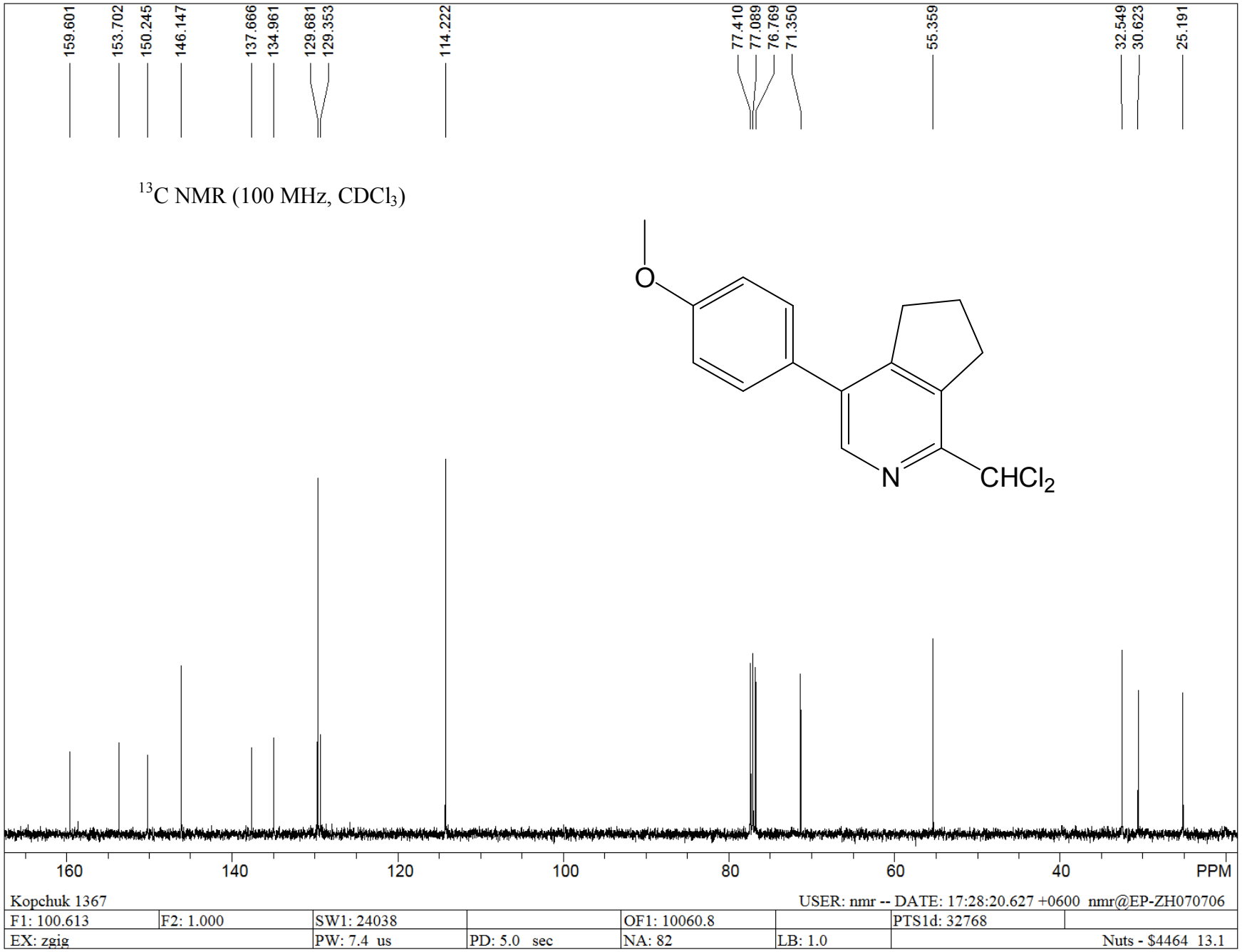
1 D. N. Kozhevnikov, N. N. Kataeva, V. L. Rusinov and O. N. Chupakhin,
Russ. Chem. Bull., *Int. Ed.*, 2004, **53**, 1295 (*Izv. Akad. Nauk, Ser. Khim.*, 2004, 1243).

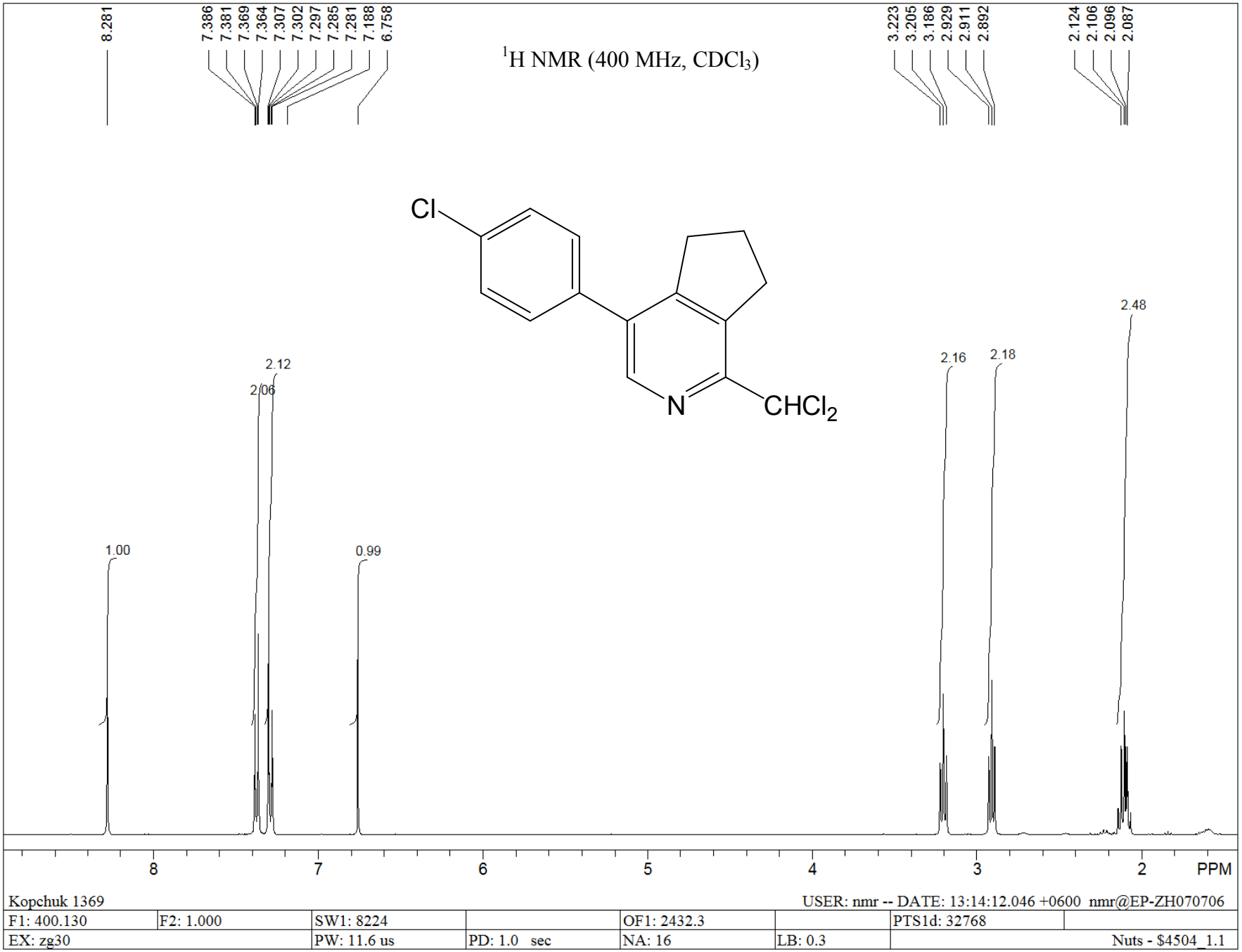

9.095
8.182
8.159
7.261
7.123
7.100
3.922
^{1}H NMR (400 MHz, $CDCl_3$)
O
N
N
N
CCl_3
0.98
2.00
2.00
2.93
9
8
7
6
5
4
PPM
Kopchuk NV96
USER: nmr -- DATE: 16:04:59.794 +0600 nmr@EP-ZH070706
F1: 400.130
F2: 1.000
SW1: 8224
OF1: 2461.4
PTS1d: 32768
EX: zg30
PW: 11.6 us
PD: 1.0 sec
NA: 8
LB: 0.3
Nuts - $4149 1.1

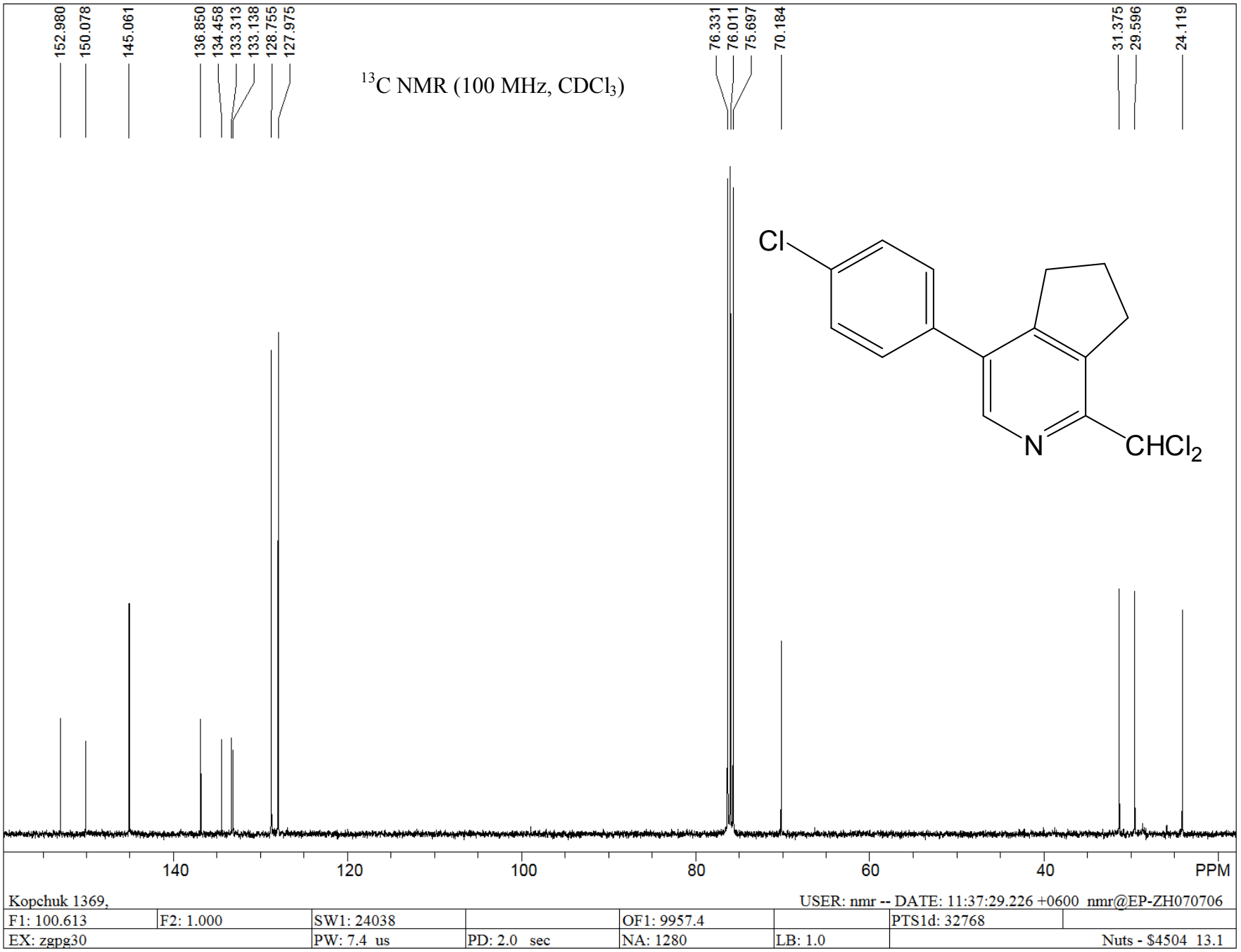

8.390
7.476
7.473
7.458
7.444
7.440
7.428
7.423
7.257
6.857
3.304
3.285
3.266
3.036
3.018
2.999
2.193
2.174
2.155
^{1}H NMR (400 MHz, $CDCl_3$)
N
$CHCl_2$
1.00
5.21
0.97
2.14
2.14
2.32
8
7
6
5
4
3
2PPM
Kopchuk NV-70-2
USER: nmr -- DATE: 16:31:26.588 +0500 nmr@EP-ZH070706
F1: 400.130
F2: 1.000
SW1: 8224
OF1: 2460.2
PTS1d: 32768
EX: zg30
PW: 11.6 us
PD: 1.0 sec
NA: 14
LB: 0.3
Nuts - $2862 1.1

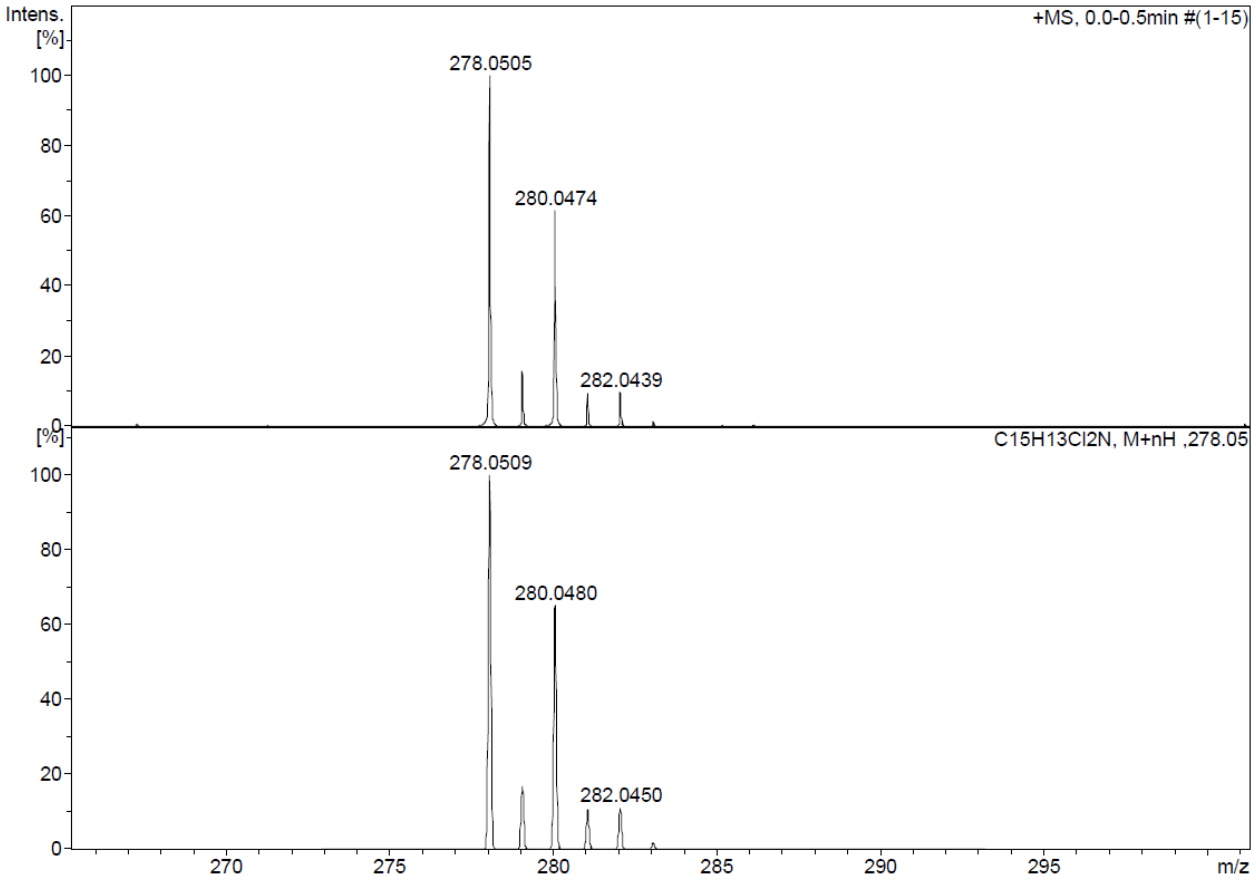

154.059
150.741
146.307
137.732
137.075
135.303
128.733
128.507
128.106
77.359
77.038
76.725
71.299
32.446
30.638
25.169
^{13}C NMR (100 MHz, $CDCl_3$)
N
$CHCl_2$
140
120
100
80
60
40
PPM
Kopchuk Cl-1
USER: nmr -- DATE: 17:15:27.224 +0600 nmr@EP-ZH070706
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10060.8
PTS1d: 32768
EX: zgig
PW: 7.4 us
PD: 5.0 sec
NA: 101
LB: 1.0
Nuts - $4480_13.1

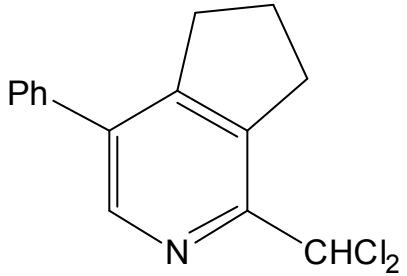

8.362
7.383
7.376
7.371
7.354
7.347
7.259
7.012
7.005
6.983
6.833
3.850
3.273
3.254
3.236
3.016
2.998
2.979
2.190
2.171
2.153
2.134
2.115
^{1}H NMR (400 MHz, $CDCl_3$)
O
N
$CHCl_2$
0.90
1.85
1.84
0.88
2.77
1.95
2.02
2.40
8
7
6
5
4
3
2
PPM
Kopchuk 1367
USER: nmr -- DATE: 17:31:41.705 +0600 nmr@EP-ZH070706
F1: 400.130
F2: 1.000
SW1: 8224
OF1: 2460.8
PTS1d: 32768
EX: zg30
PW: 11.6 us
PD: 1.0 sec
NA: 29
LB: 0.3
Nuts - $4505 1.1

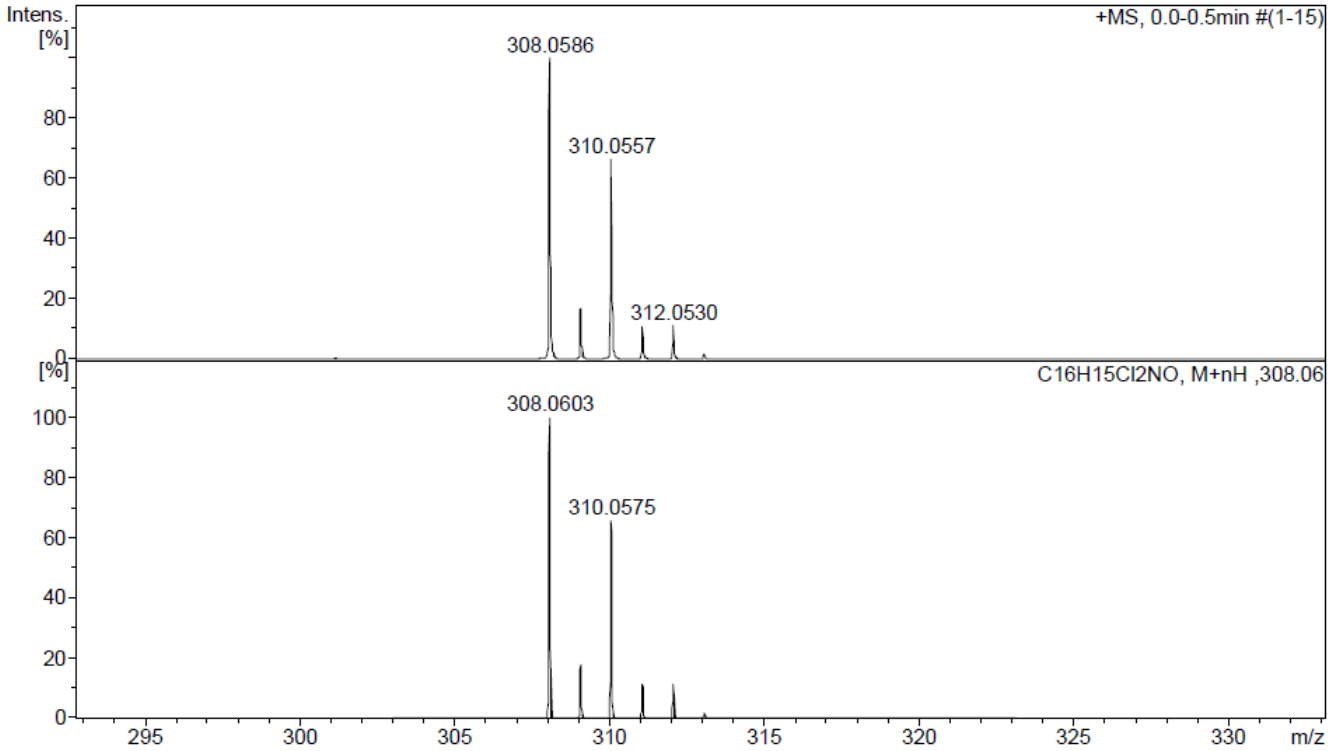

159.601
153.702
150.245
146.147
137.666
134.961
129.681
129.353
114.222
77.410
77.089
76.769
71.350
55.359
32.549
30.623
25.191
13C NMR (100 MHz, CDCl3)
O
N
CHCl2
160
140
120
100
80
60
40
PPM
Kopchuk 1367
USER: nmr -- DATE: 17:28:20.627 +0600 nmr@EP-ZH070706
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 10060.8
PTS1d: 32768
EX: zgig
PW: 7.4 us
PD: 5.0 sec
NA: 82
LB: 1.0
Nuts - $4464 13.1

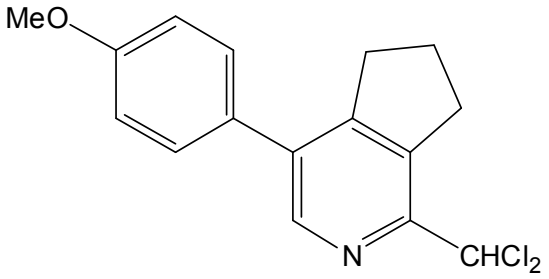

8.281
7.386
7.381
7.369
7.364
7.307
7.302
7.297
7.285
7.281
7.188
6.758
3.223
3.205
3.186
2.929
2.911
2.892
2.124
2.106
2.096
2.087
^{1}H NMR (400 MHz, $CDCl_3$)
Cl
N
$CHCl_2$
1.00
2.12
2.06
0.99
2.16
2.18
2.48
8
7
6
5
4
3
2
PPM
Kopchuk 1369
USER: nmr -- DATE: 13:14:12.046 +0600 nmr@EP-ZH070706
F1: 400.130
F2: 1.000
SW1: 8224
OF1: 2432.3
PTS1d: 32768
EX: zg30
PW: 11.6 us
PD: 1.0 sec
NA: 16
LB: 0.3
Nuts - $4504_1.1

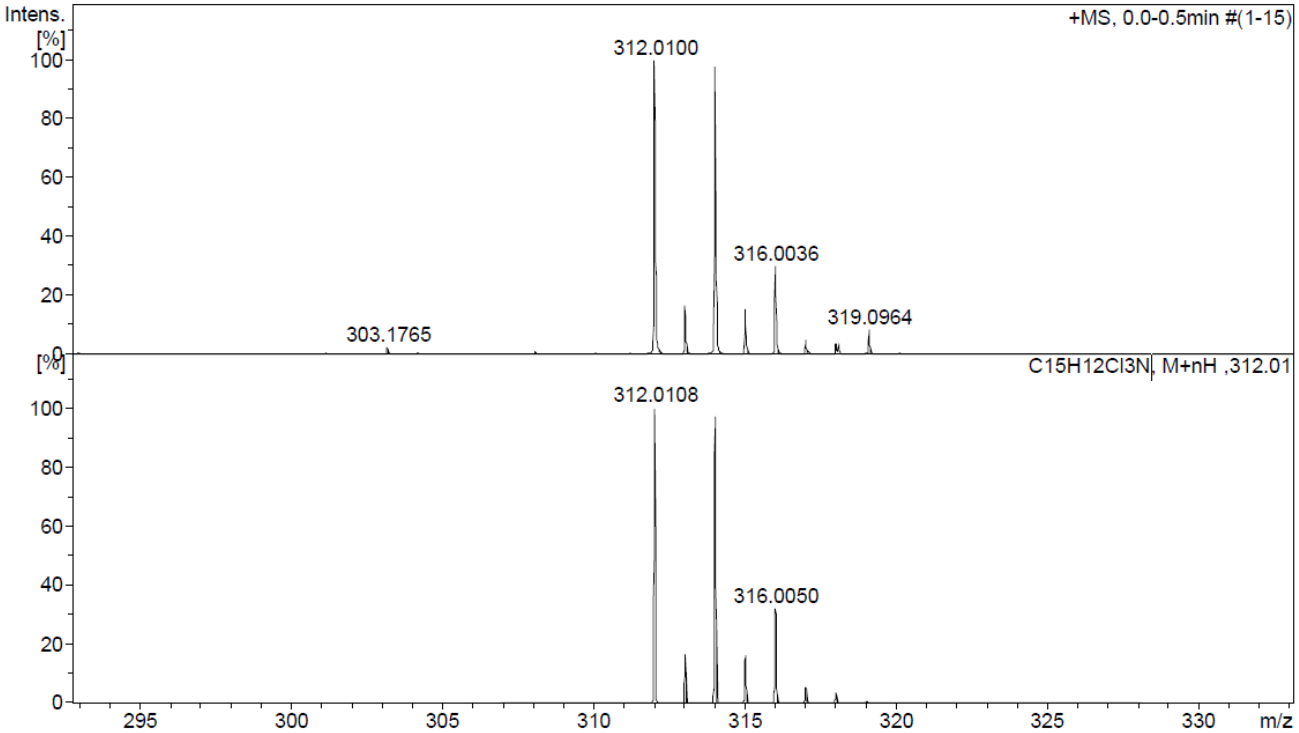

152.980
150.078
145.061
136.850
134.458
133.313
133.138
128.755
127.975
76.331
76.011
75.697
70.184
31.375
29.596
24.119
^{13}C NMR (100 MHz, $CDCl_3$)
Cl
N
$CHCl_2$
140
120
100
80
60
40
PPM
Kopchuk 1369,
USER: nmr -- DATE: 11:37:29.226 +0600 nmr@EP-ZH070706
F1: 100.613
F2: 1.000
SW1: 24038
OF1: 9957.4
PTS1d: 32768
EX: zgpg30
PW: 7.4 us
PD: 2.0 sec
NA: 1280
LB: 1.0
Nuts - $4504 13.1

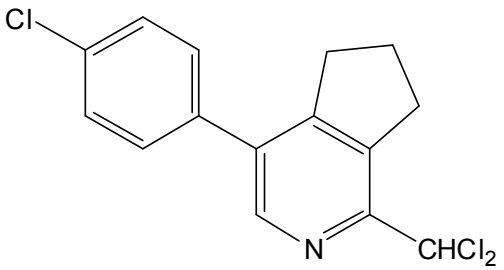

Intens.
[%]
+MS, 0.0-0.5min #(1-15)
278.0505
280.0474
282.0439
[%]
C15H13Cl2N, M+nH ,278.05
278.0509
280.0480
282.0450
100
80
60
40
20
0
270
275
280
285
290
295
m/z


Ph
N
CHCl2


Intens.
[%]
+MS, 0.0-0.5min #(1-15)
308.0586
310.0557
312.0530
C16H15Cl2NO, M+nH ,308.06
308.0603
310.0575
m/z


MeO
N
CHCl2


Intens.
[%]
+MS, 0.0-0.5min #(1-15)
312.0100
316.0036
319.0964
303.1765
C15H12Cl3N, M+nH ,312.01
312.0108
316.0050
m/z


Cl
N
CHCl2