Supporting Information for:

Total Synthesis of the *Aspidosperma* Alkaloid (±)-Subincanadine F via a Titanium-Mediated Intramolecular Nucleophilic Acyl Substitution (INAS) Strategy

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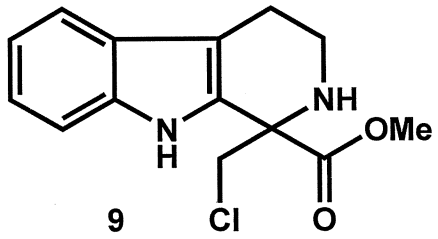
Methods and Materials

Unless otherwise stated, all non-aqueous reactions were carried out under an atmosphere of dry nitrogen in dried glassware. When necessary, solvents and reagents were dried prior to use. Tetrahydrofuran, diethyl ether, dichloromethane, benzene, and toluene were dried using a solvent purification system. Commercially available starting materials and reagents were used as received. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel plates with UV indicator. Visualization was accomplished by irradiation under a 254 nm UV lamp followed by staining with either an aqueous solution of ceric ammonium molybdate (CAM) or iodine. Flash column chromatography was performed using a forced flow of the indicated solvent system on silica gel (230-400 mesh).

^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz spectrometer at 500 and 125 MHz, respectively. Chemical shifts are reported relative to either chloroform (δ 7.26) or methanol (δ 3.31) for ^{1}H NMR and either chloroform (δ 77.0) or methanol (δ 49.15) for ^{13}C NMR. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet,), coupling constants (Hz), and number of protons. IR spectra were recorded on a FT-IR spectrometer with an attenuated total reflectance (ATR) head. High-resolution mass spectra (HRMS) in CI and ESI modes were obtained on a GC-TOF mass spectrometer.


NH
N
H
OMe
O
Cl

9

0.99
1.00
1.01
1.10
1.02
0.92
2.73
1.01
1.88
1.95
9.0
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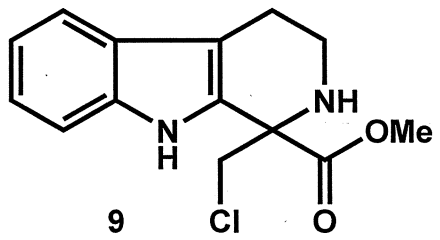
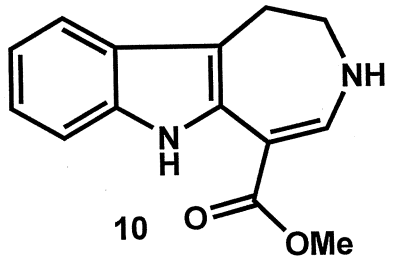
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


NH
N
H
OMe
Cl
O

9

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)


NH
N
H
O
OMe

10

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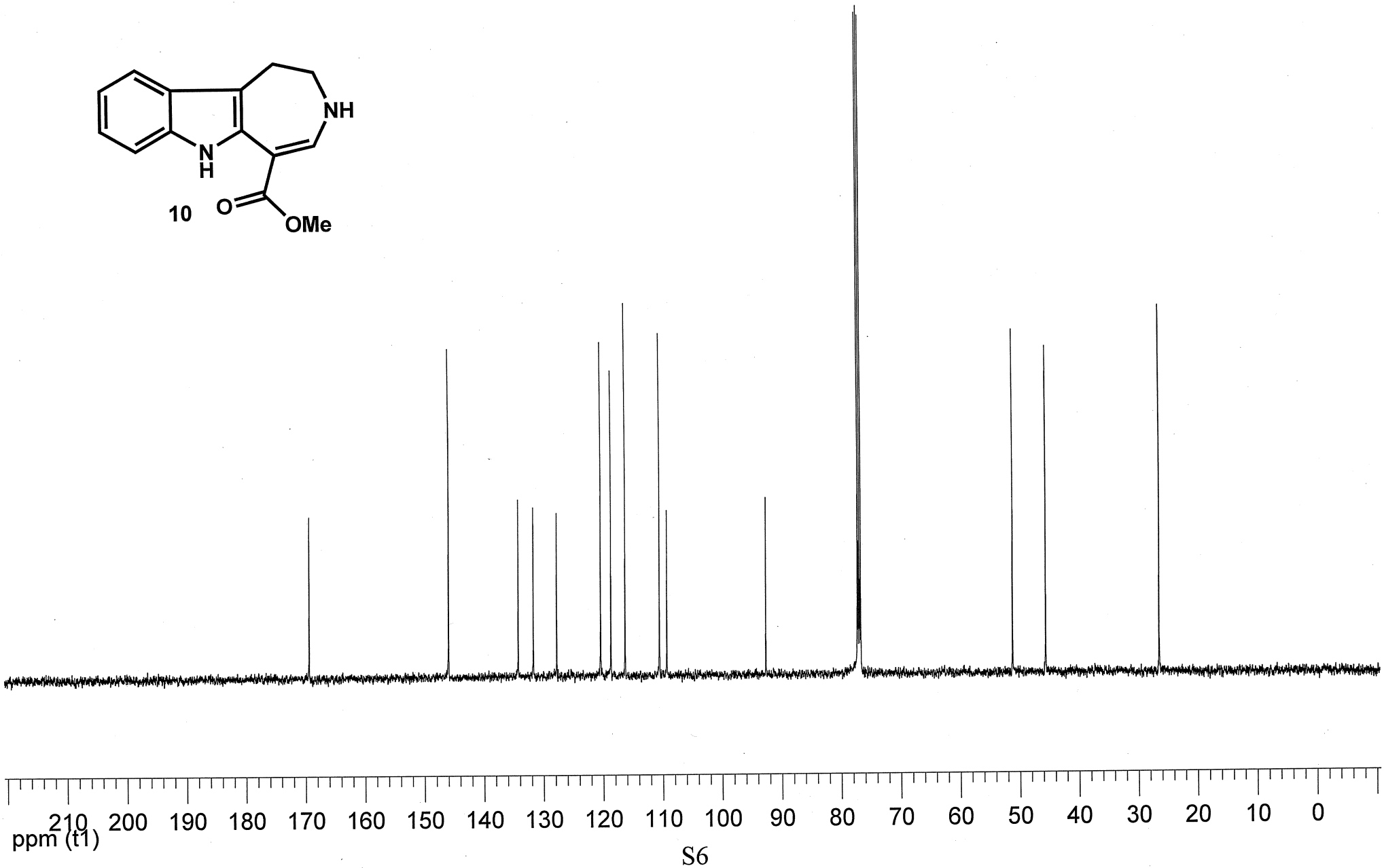
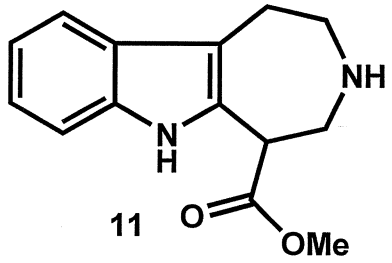
1.00
0.99
1.01
2.07
1.00
2.82
1.96
1.93
ppm (t1)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


NH
N
H
O
OMe
10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)



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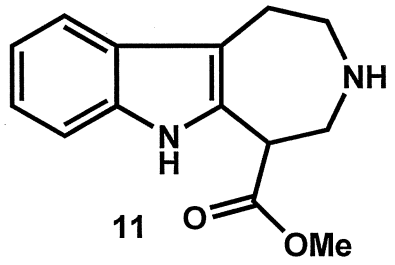
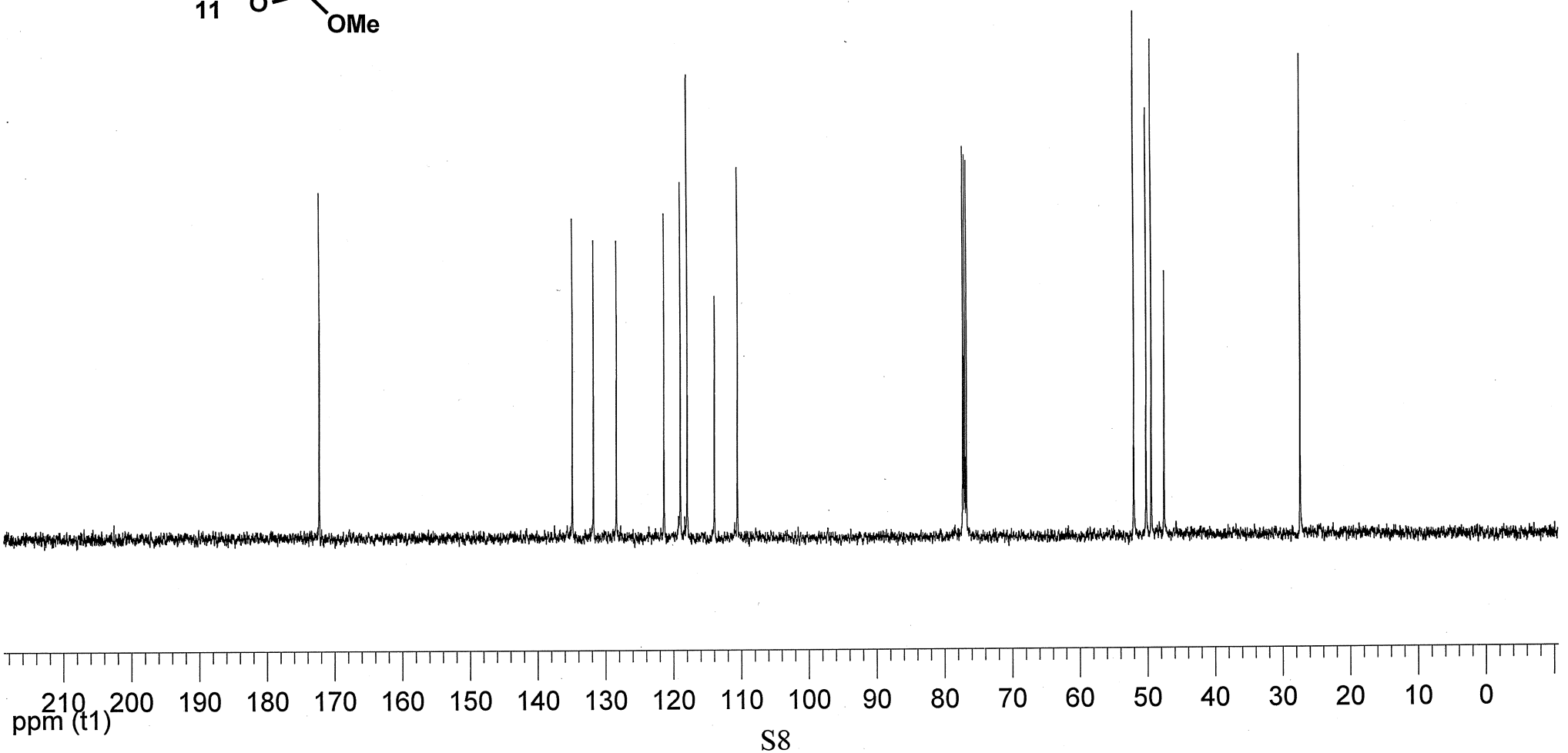
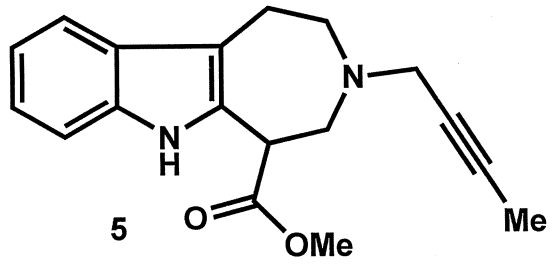

NH
N
H
O
OMe

11


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)


N
H
O
OMe
N
Me

5

0.91
1.00
1.06
2.11
0.92
2.97
1.70
1.10
1.11
3.95
2.95
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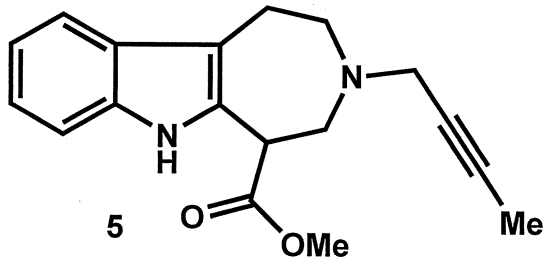
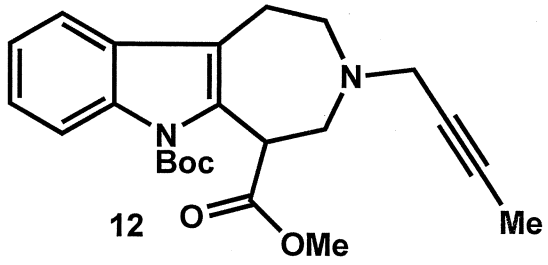
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


N
H
O
OMe
N
Me

5

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)


N
Boc
O
OMe
Me

12

1.00
1.07
3.27
1.04
3.00
1.15
2.19
1.20
1.15
2.41
1.14
3.12
9.06
ppm (t1)
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8.0
7.0
6.0
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4.0
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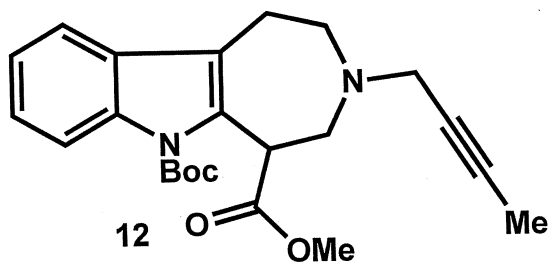
1.0
0.0


N
Boc
O
OMe
Me

12

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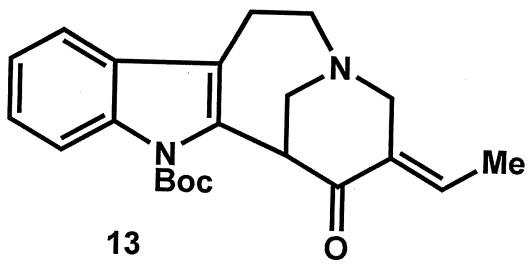
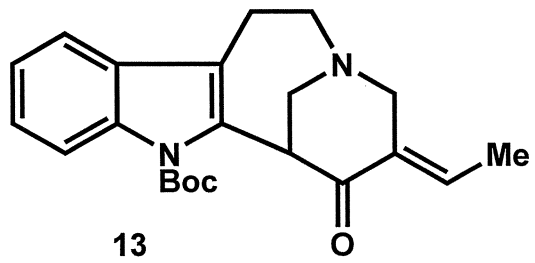
ppm (t1)


N
N
Boc
Me
O

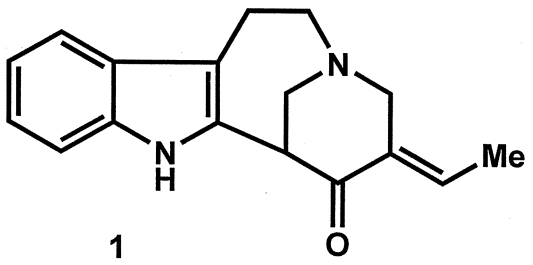
13

1.05
1.18
1.26
1.03
0.96
2.24
1.29
1.24
1.22
1.38
1.24
1.21
9.61
3.29
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


N
N
Boc
Me
O

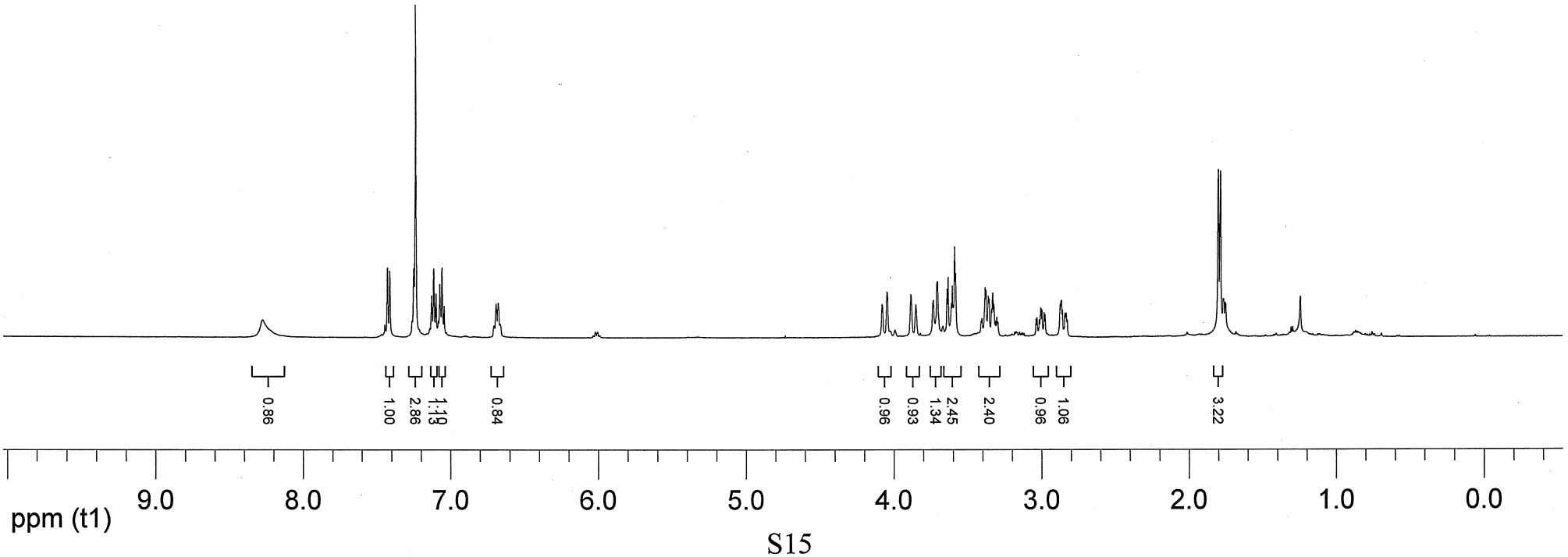
13

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)


N
H
Me
O

1

(In $CDCl_3$)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2.40
0.96
1.06
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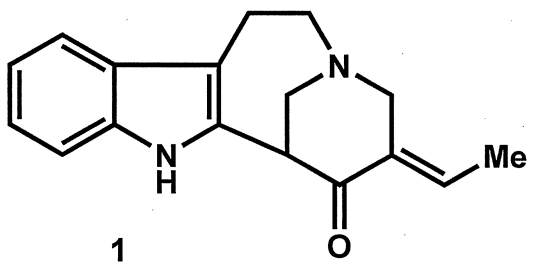
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


N
H
Me
O

1

(In CD_3OD)

1.09
1.37
1.28
1.28
0.89
0.90
1.16
3.80
2.46
2.34
1.20
1.37
3.44
ppm (t1)
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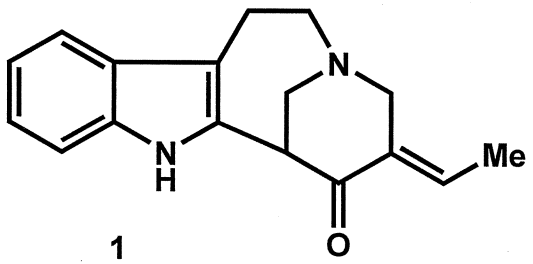
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


N
H
Me
O

1

(In $CDCl_3$)

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm (t1)