Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supplementary Information

Revitalizing the aromatic aza-Claisen rearrangement: implications for the mechanism of 'on-water' catalysis.

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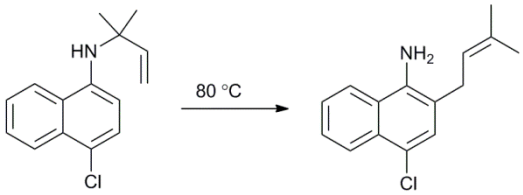
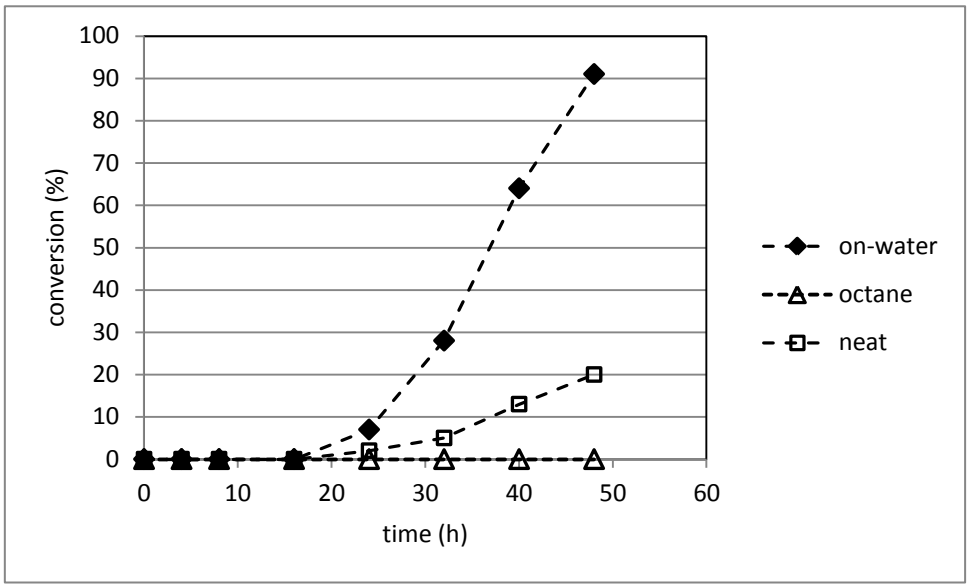
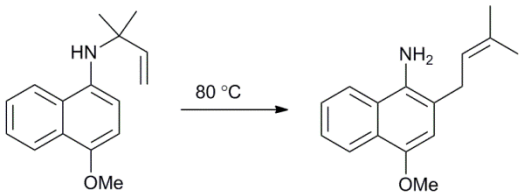
General Experimental Details:

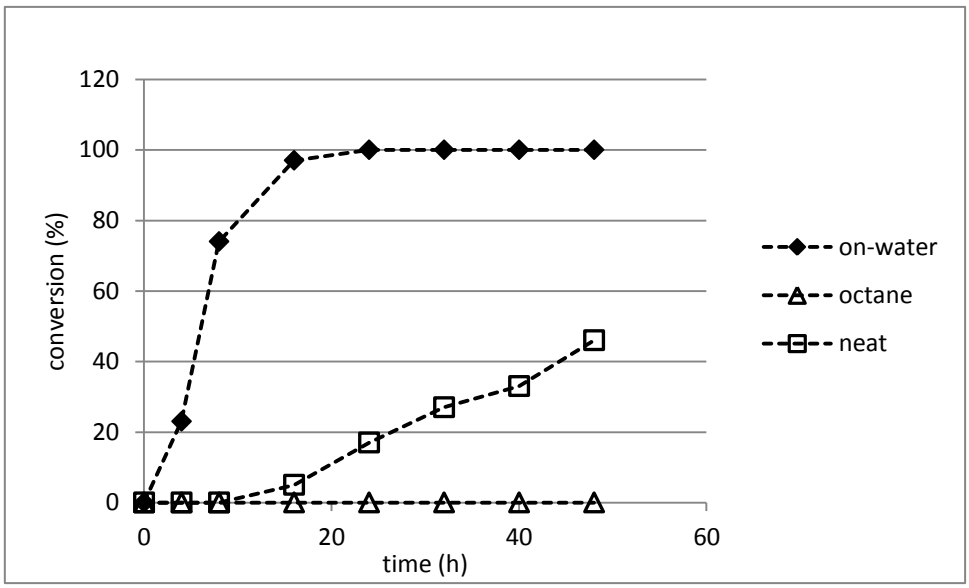
All solvents and reagents were used as received from commercial sources. Melting points were determined using a Stanford Research Systems Optimelt automated melting point system and are uncorrected. Infrared spectra were acquired neat on a Bruker Alpha-E ATR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ASCEND 500 (^{1}H frequencies 500 MHz; ^{13}C frequencies 125 MHz), a Bruker AVANCE DPX300 (^{1}H frequencies 300 MHz; ^{13}C frequencies 75 MHz) or a Bruker AVANCE DPX200 (^{1}H frequencies 200 MHz; ^{13}C frequencies 50 MHz). ^{1}H chemical shifts are expressed as parts per million (ppm) with residual chloroform (δ 7.26) as reference and are reported as chemical shift (δ_H); relative integral; multiplicity (s singlet, br broad, d doublet, t triplet, dd doublet of doublets, dt doublet of triplets, q quartet, m multiplet); and coupling constants (*J*) reported in Hz. ^{13}C NMR chemical shifts are expressed as parts per million (ppm) with residual chloroform (δ 77.1) as internal reference and are reported as chemical shift (δ_C); multiplicity (assigned from DEPT experiments). High resolution mass spectra were recorded on a Bruker ApexII Fourier Transform Ion Cyclotron Resonance mass spectrometer with a 7.0 T magnet, fitted with an off-axis Analytical electrospray source.

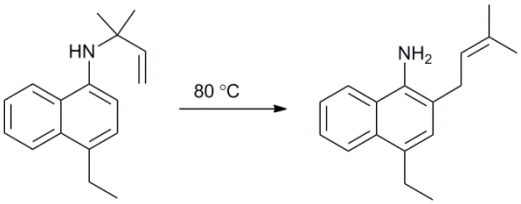
Comparative Rate Plots for the Aza-Claisen Rearrangement of Compounds 2b, 2c, 2d, 9a, 9b, 9c:

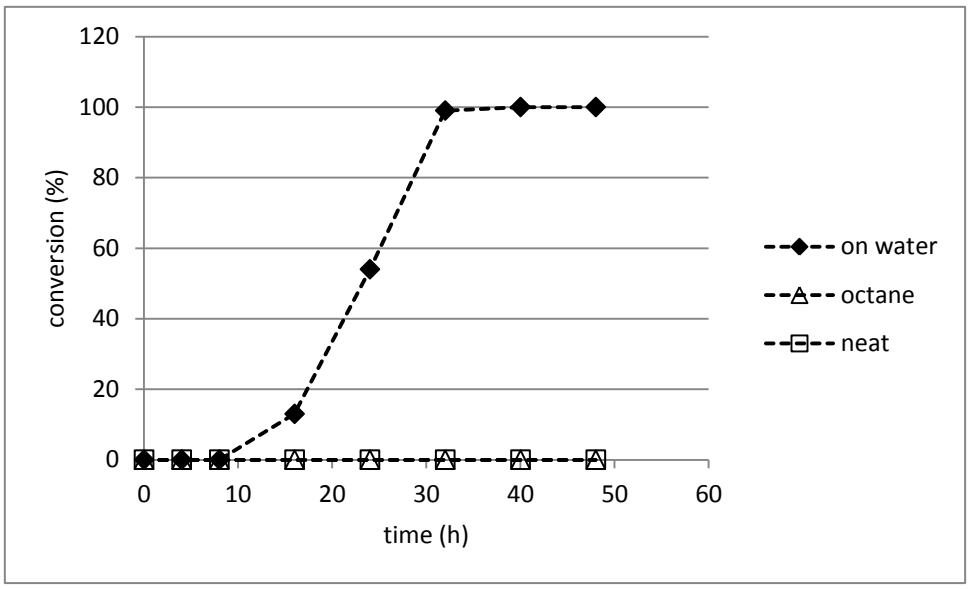


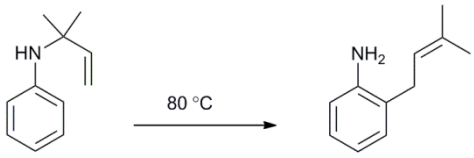


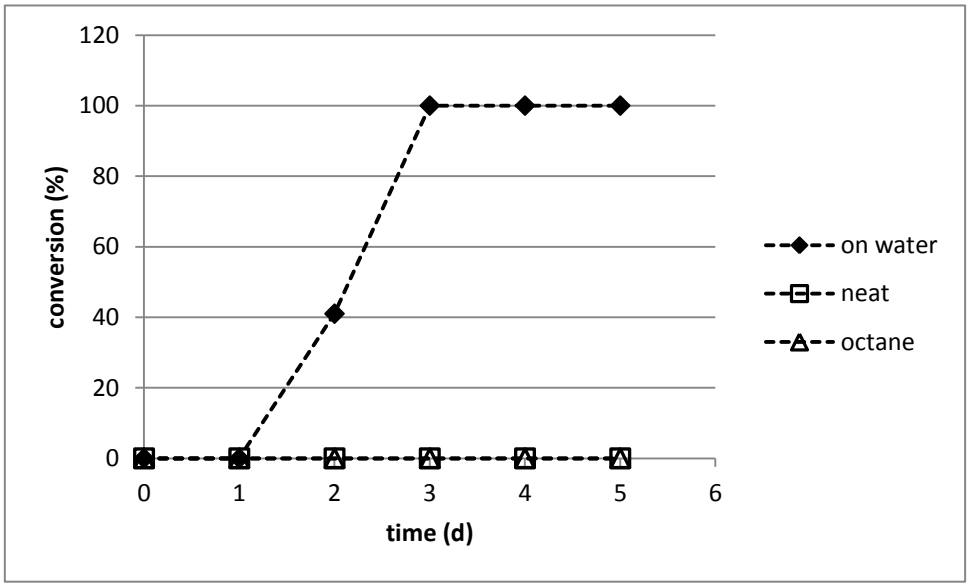


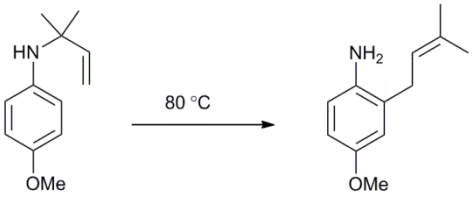


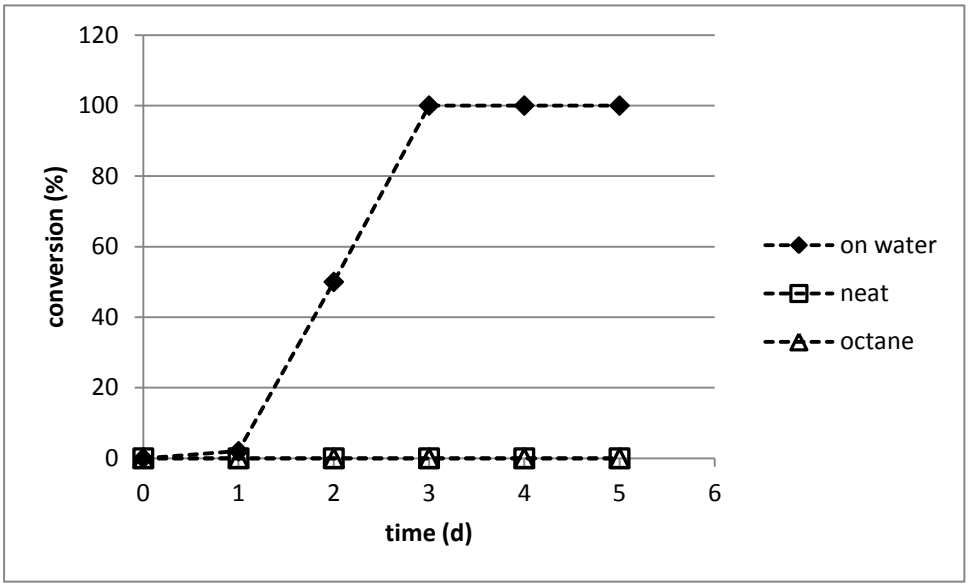


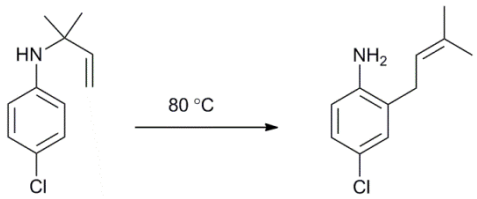


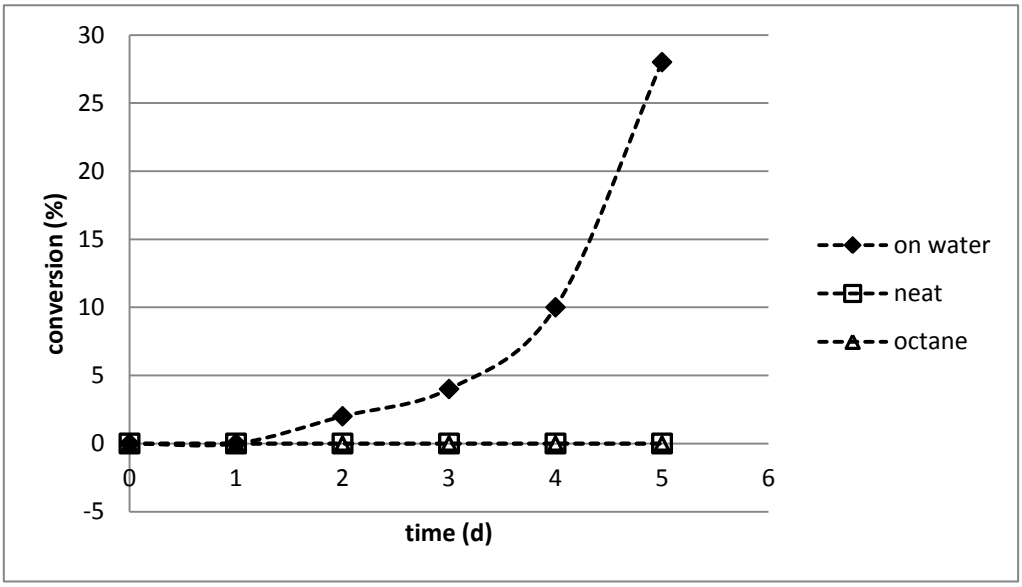


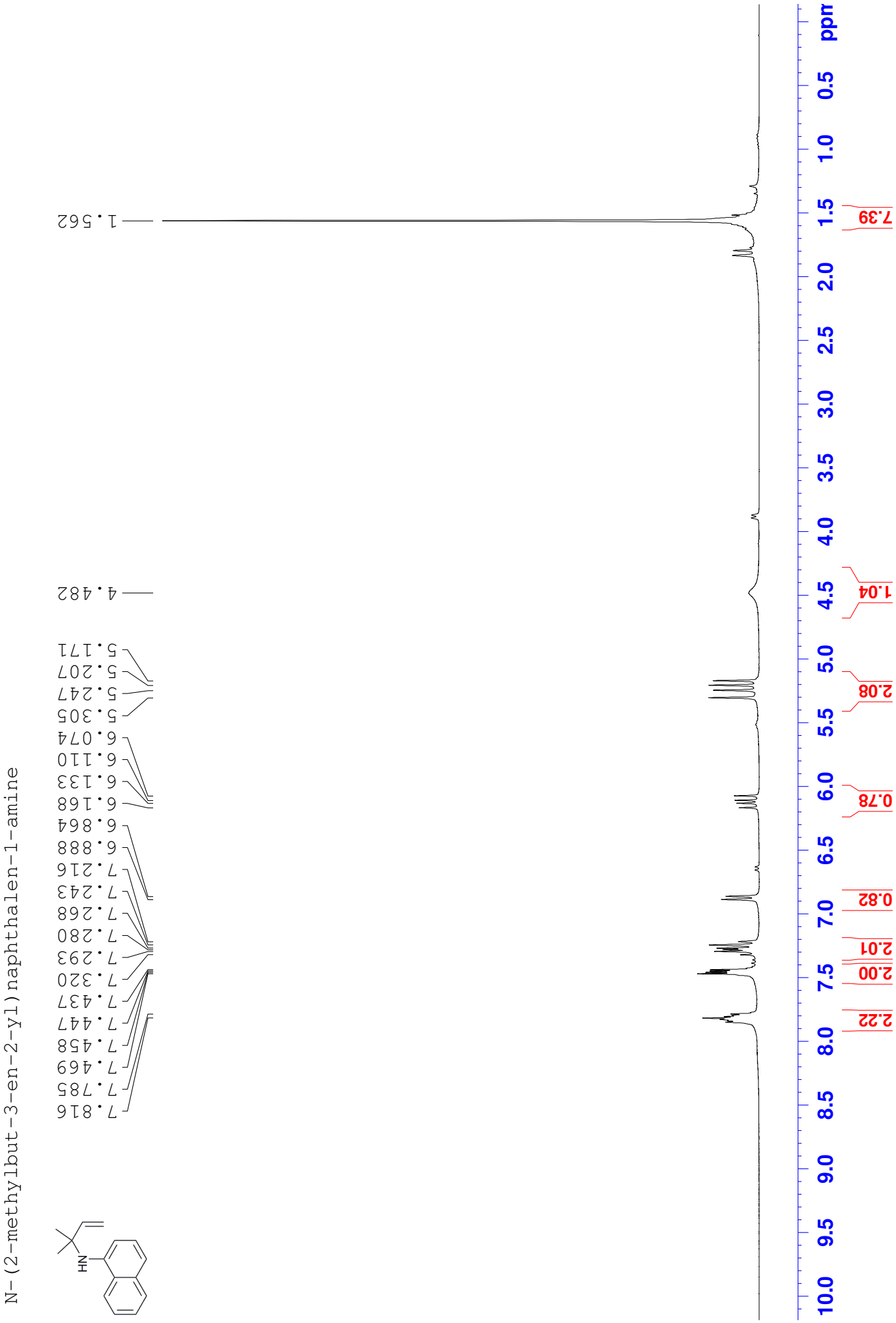


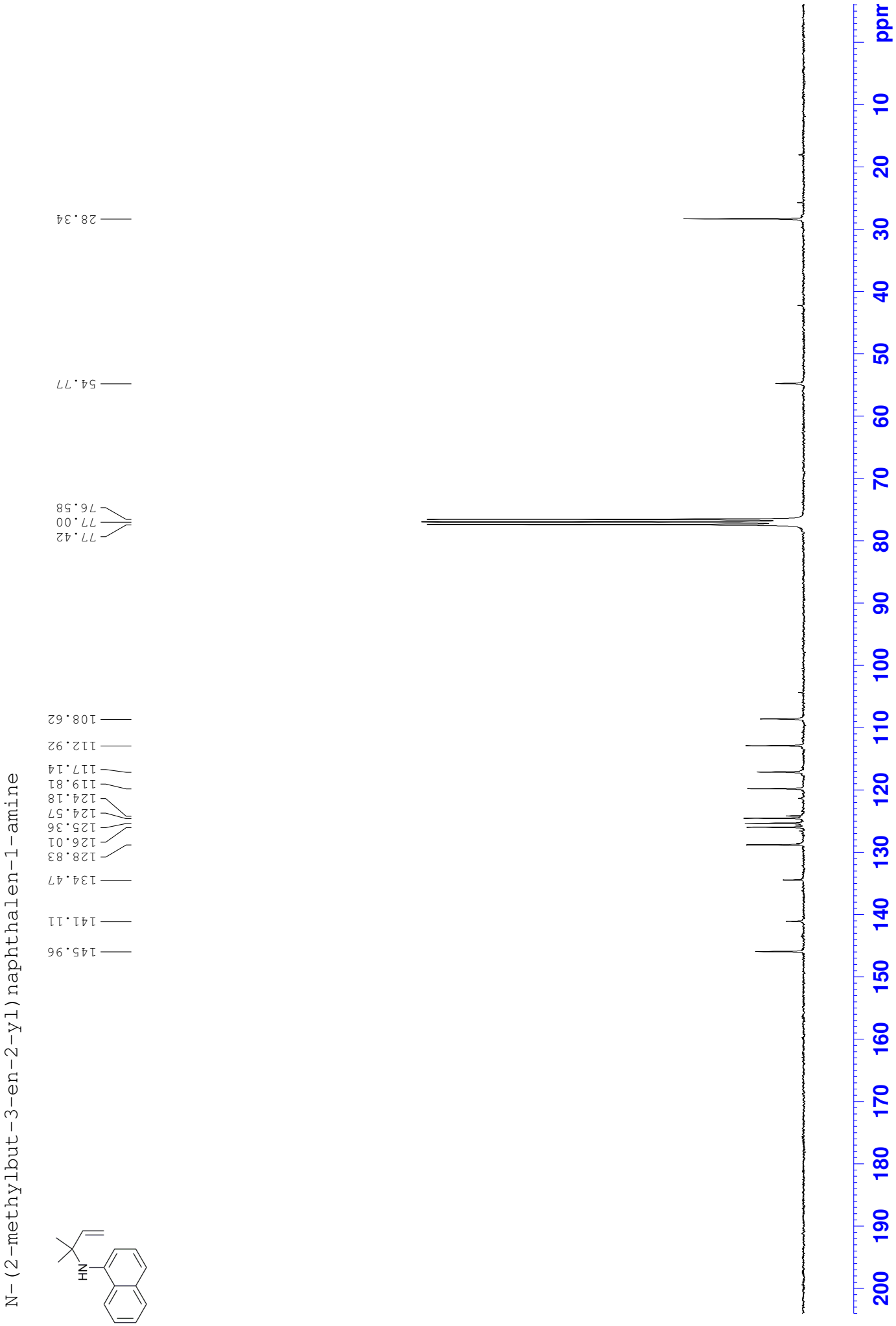


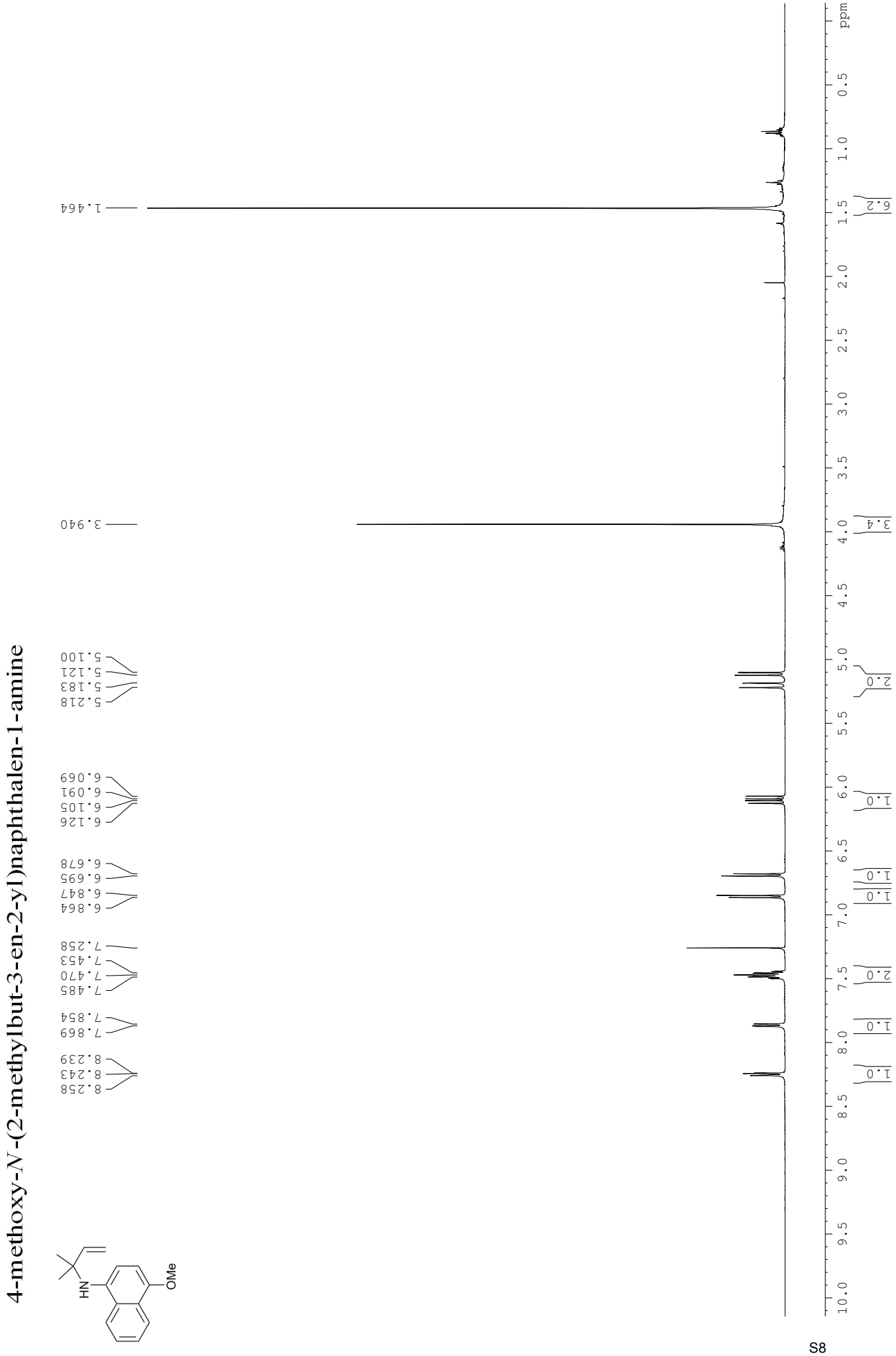


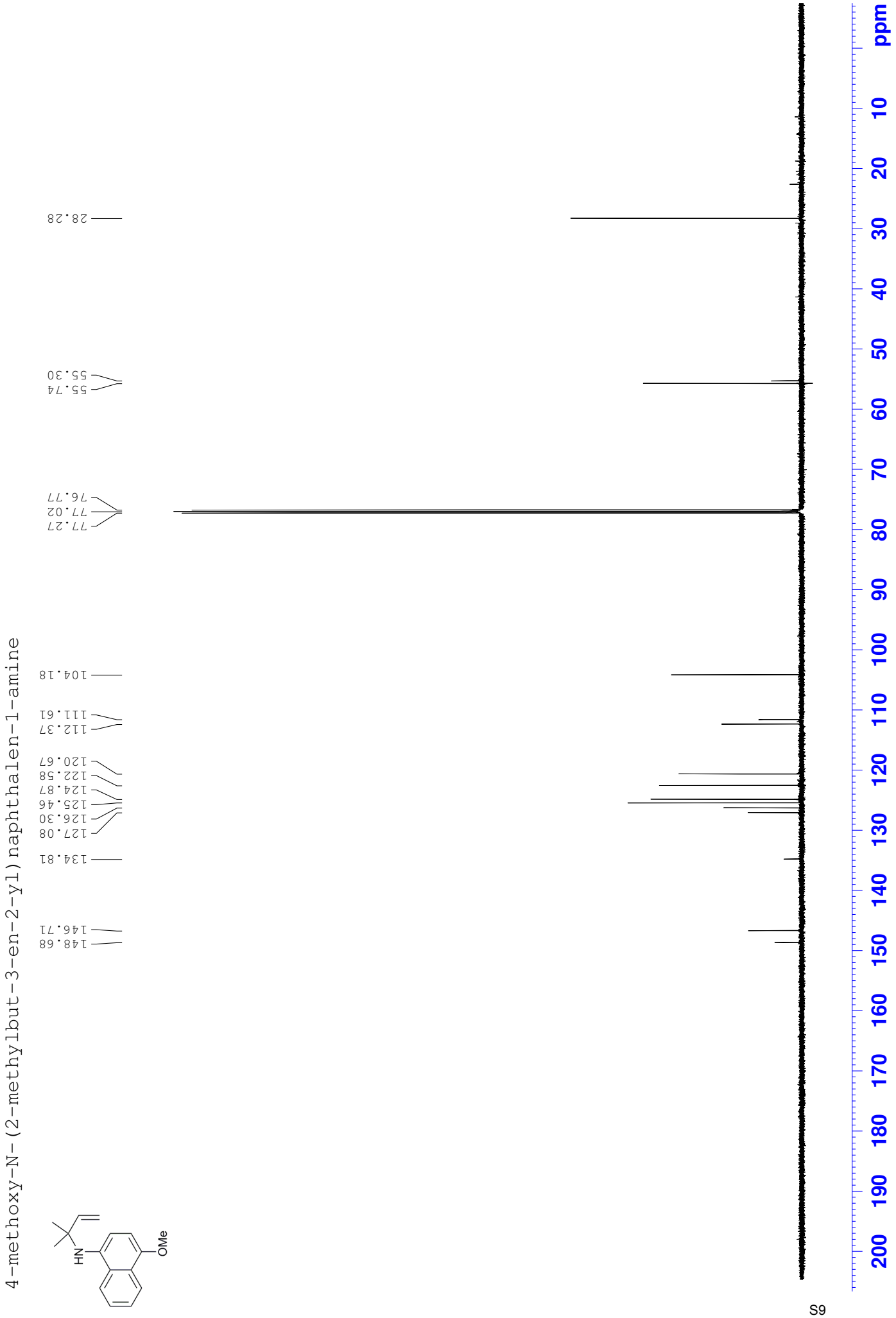


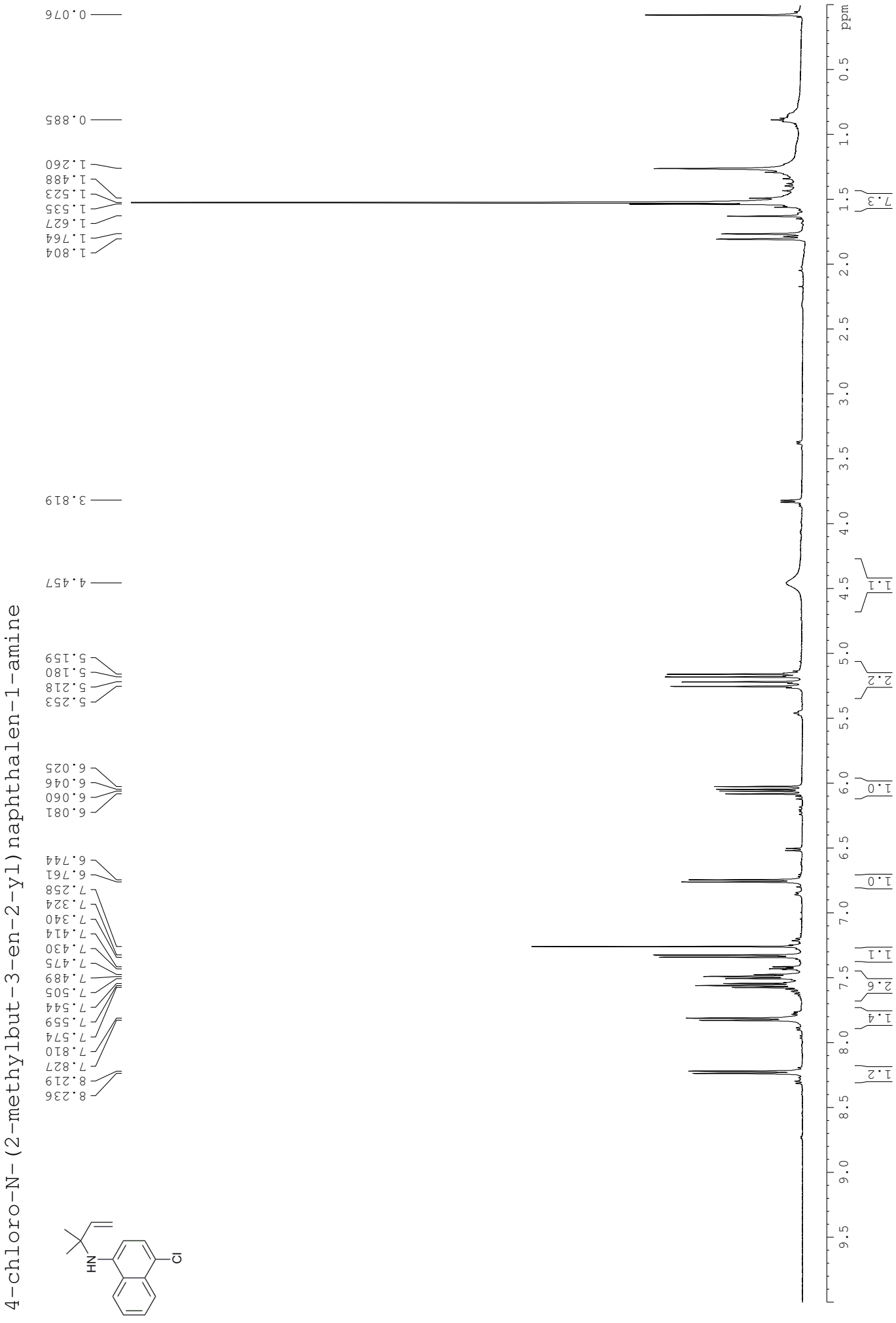


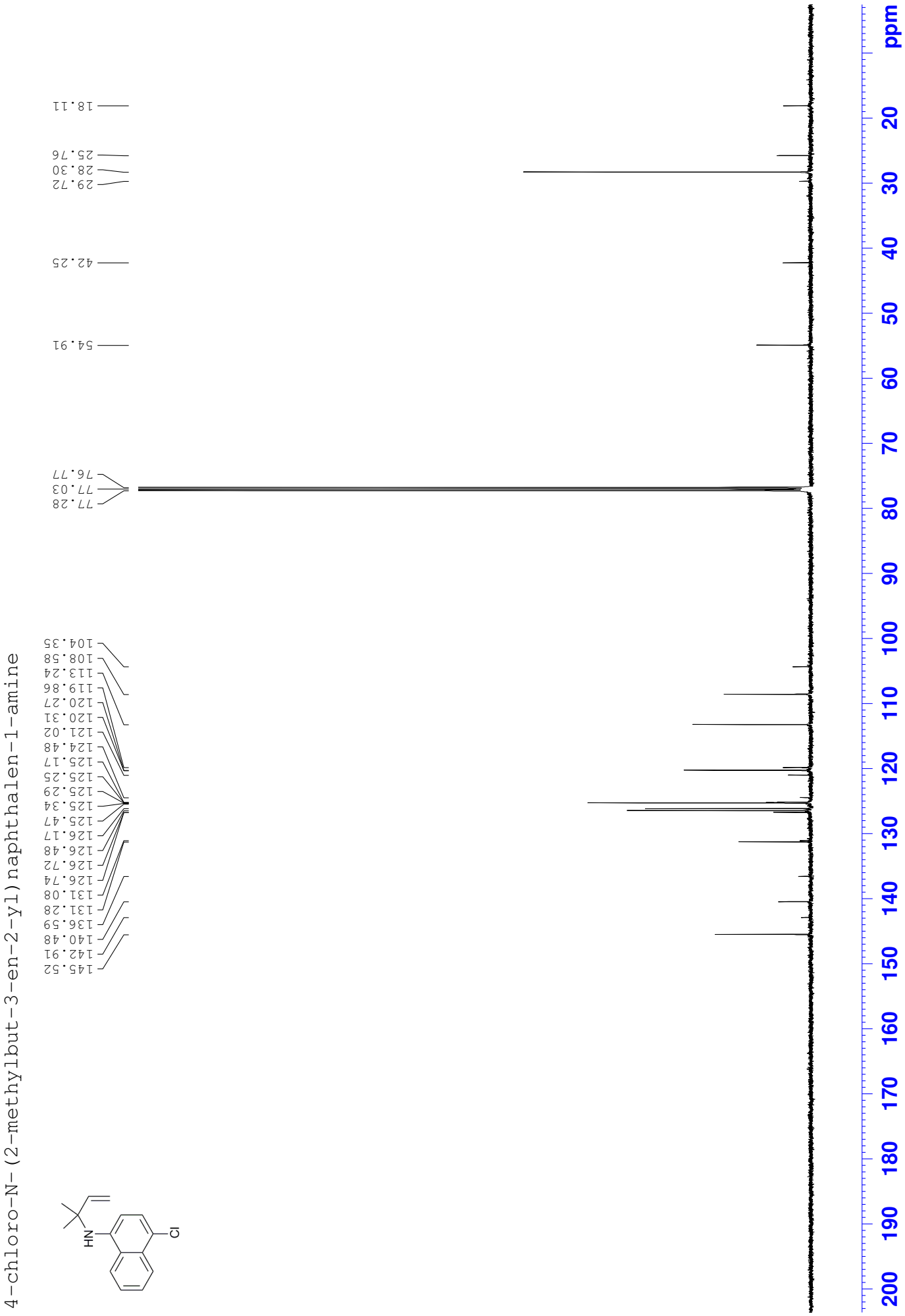


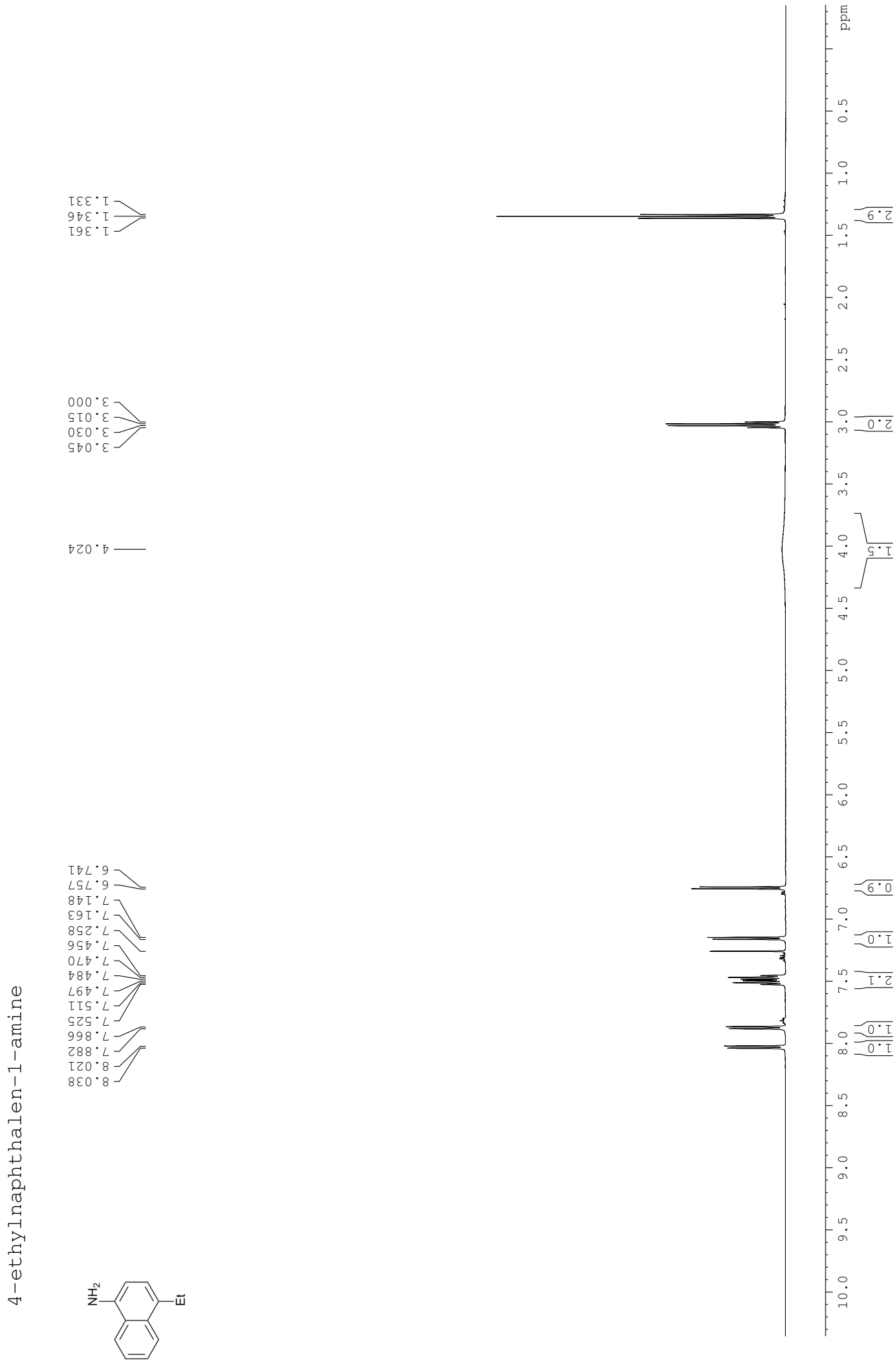


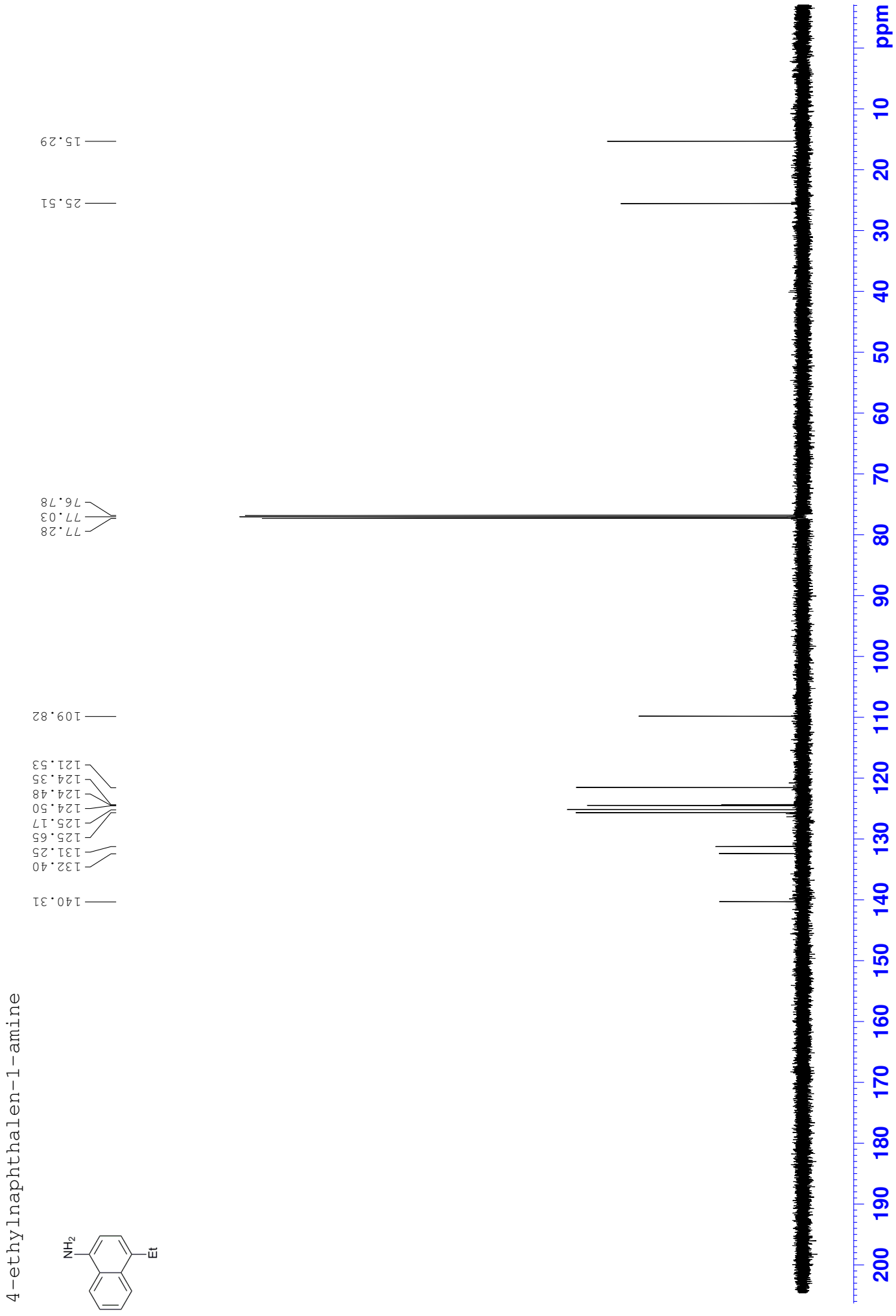


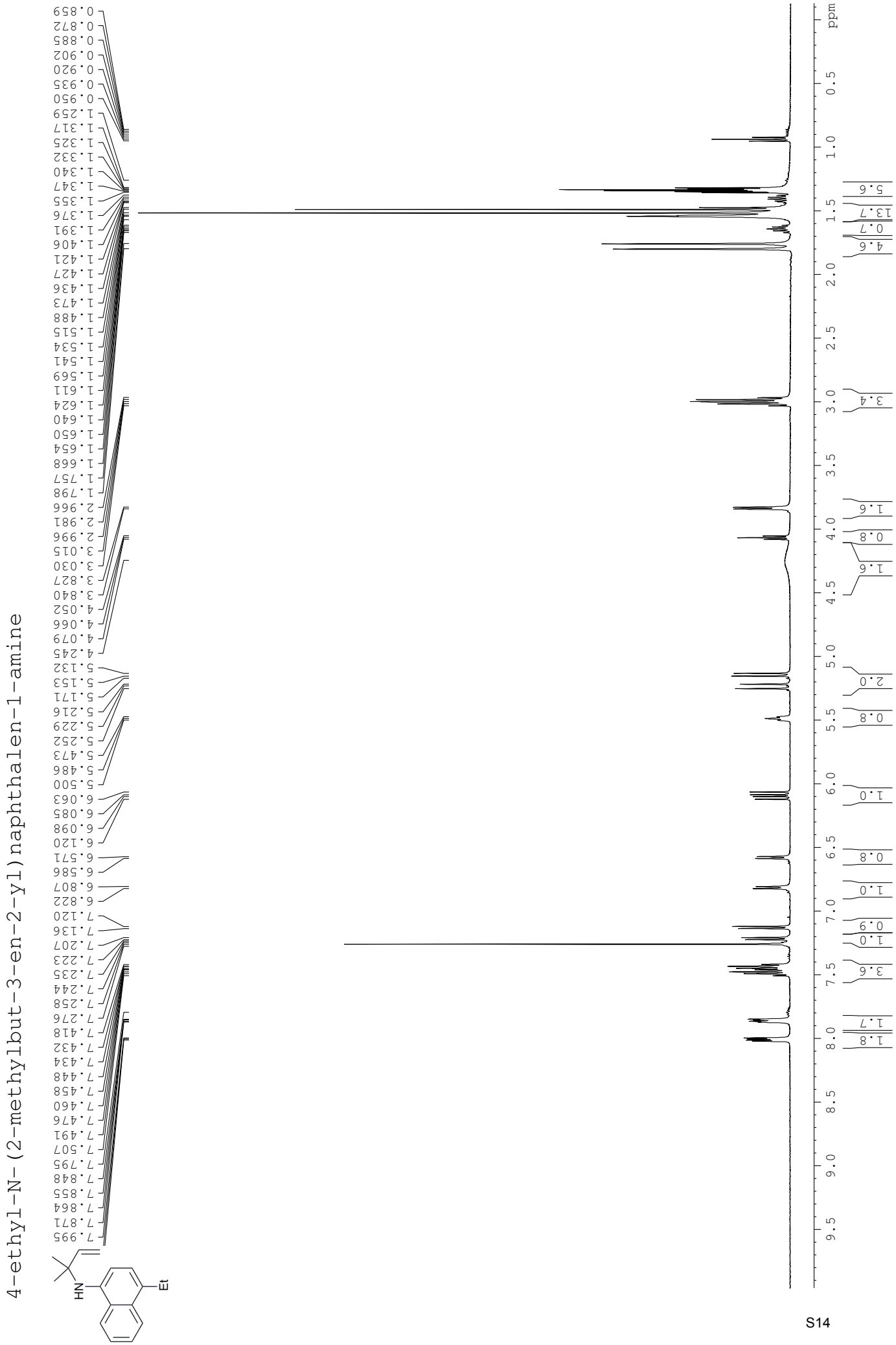


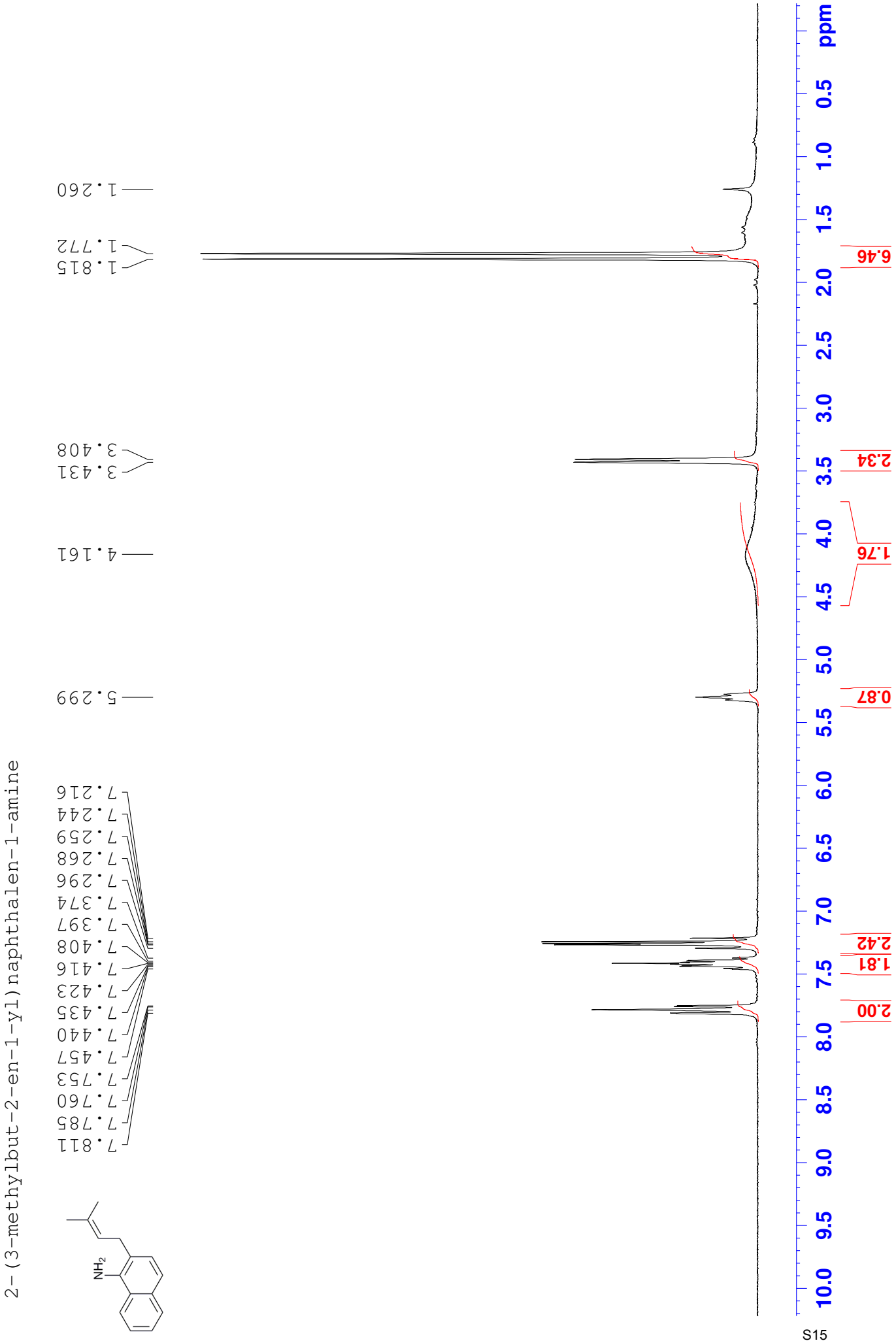


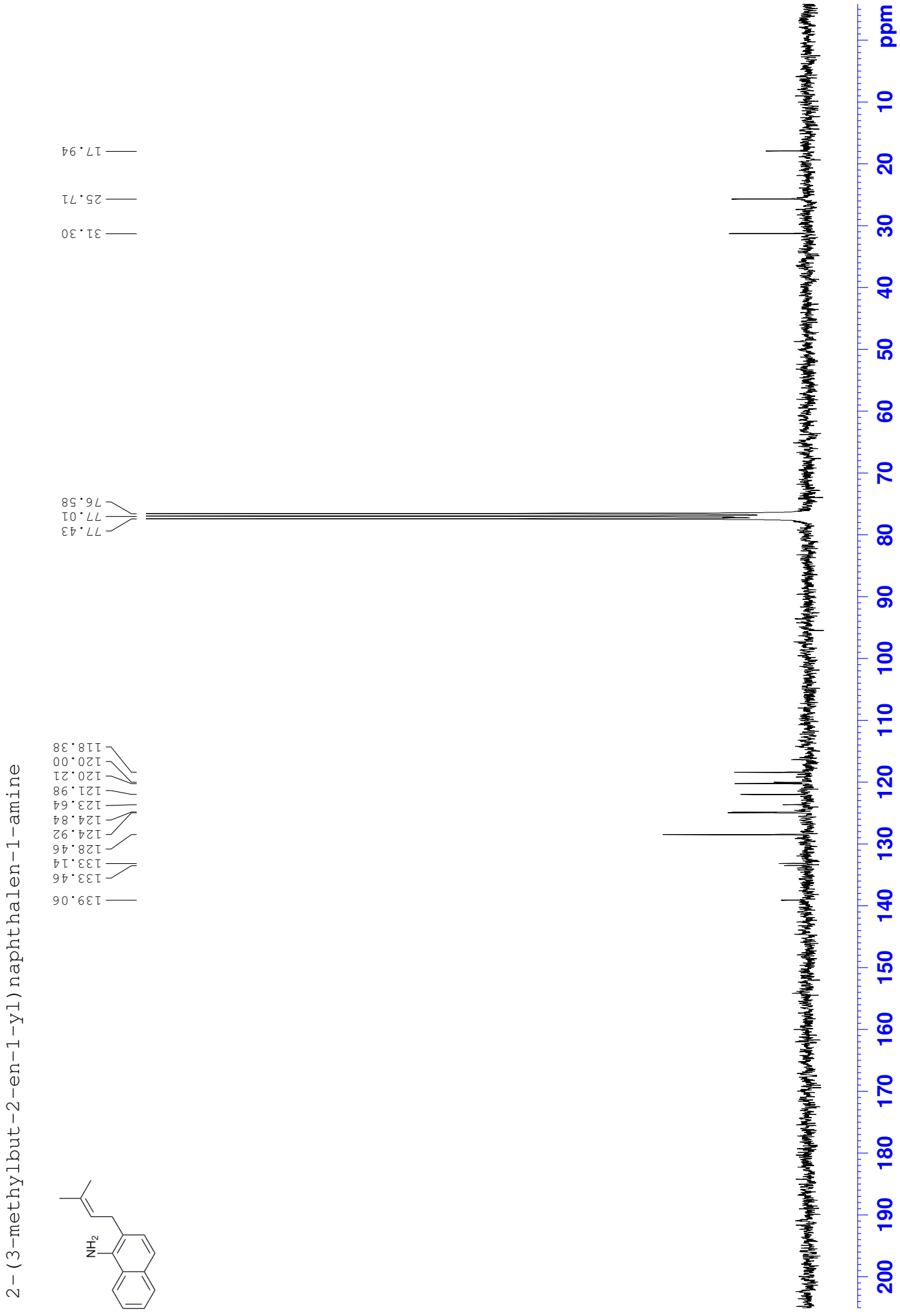


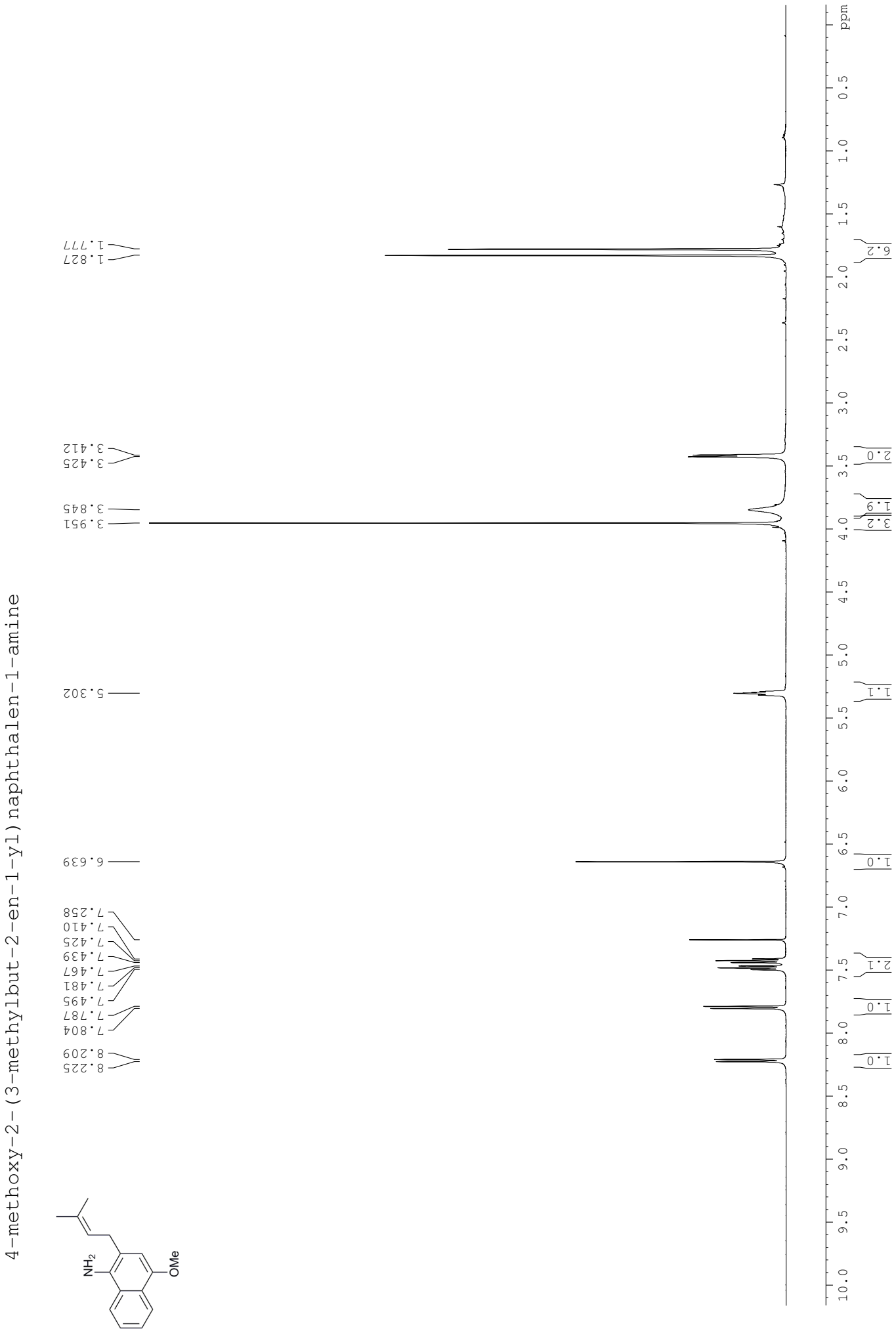


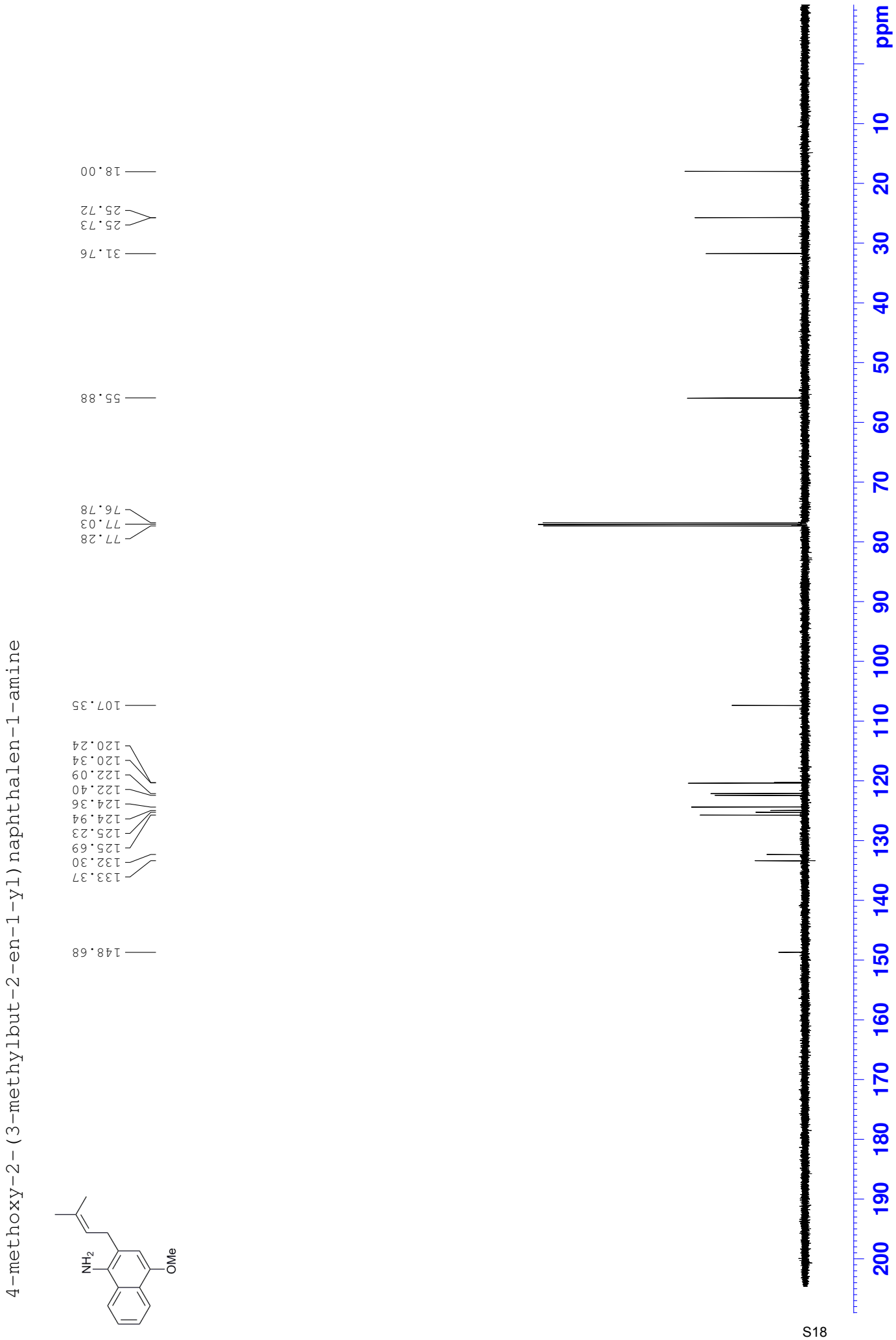








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NH2
OMe
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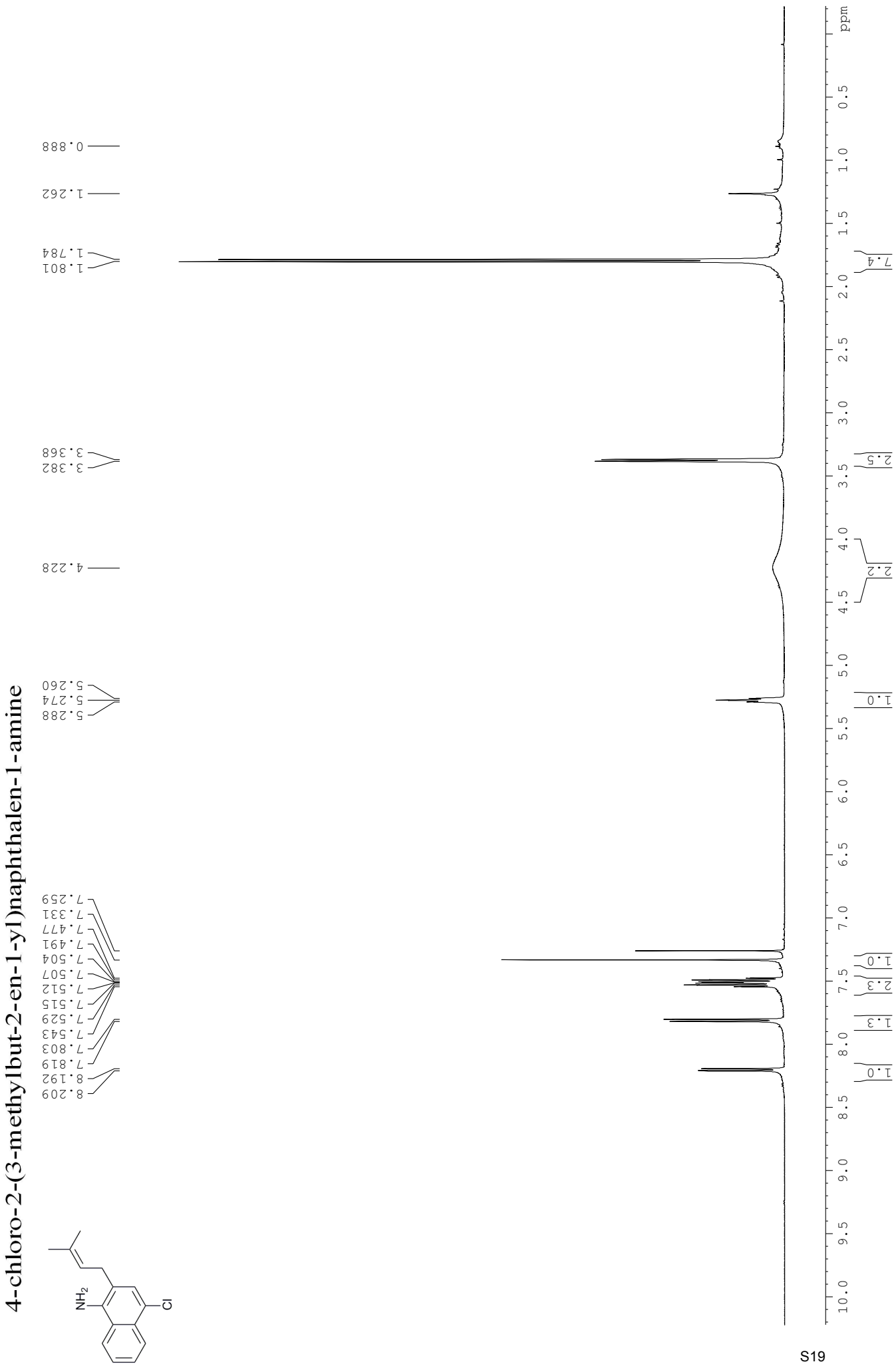
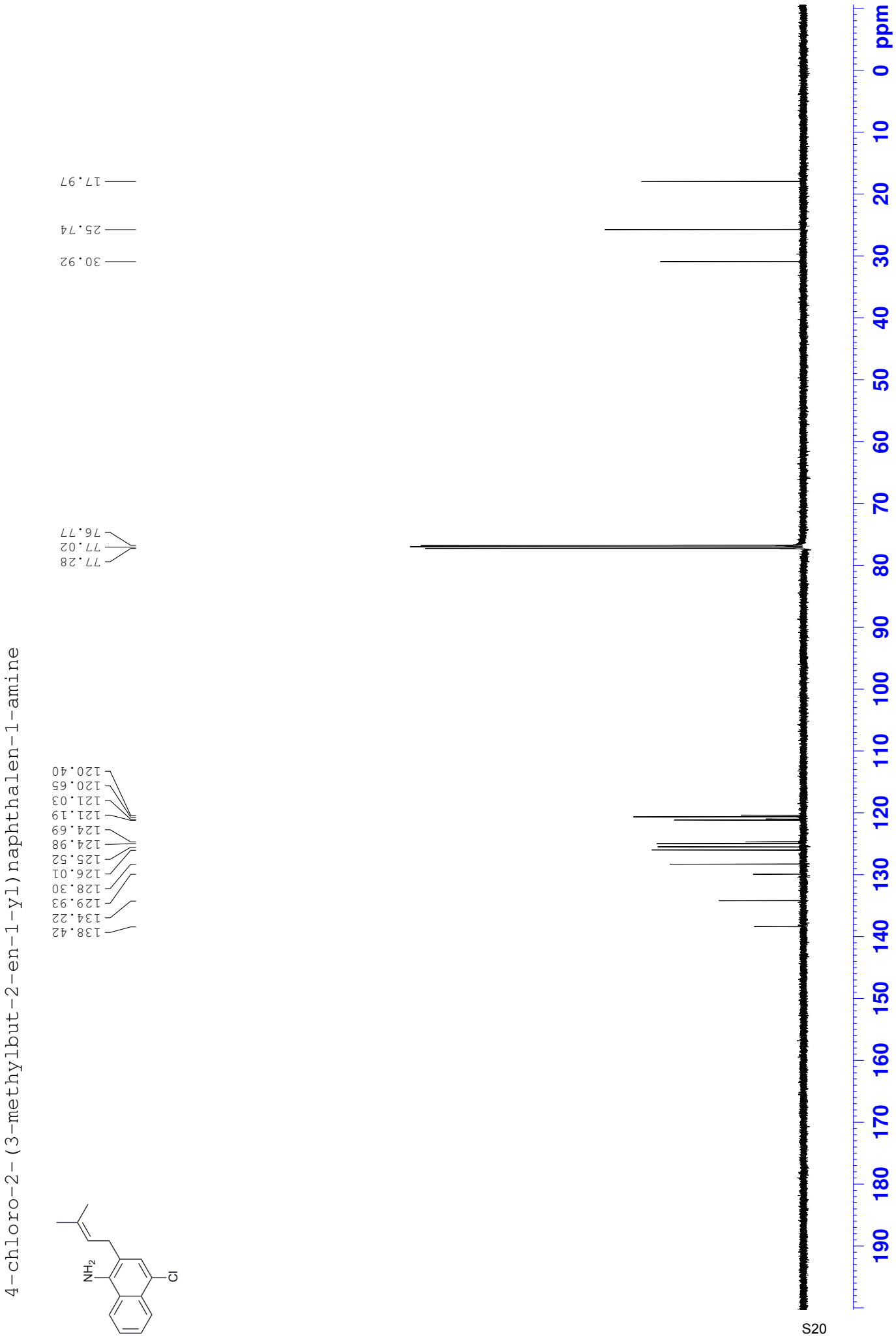
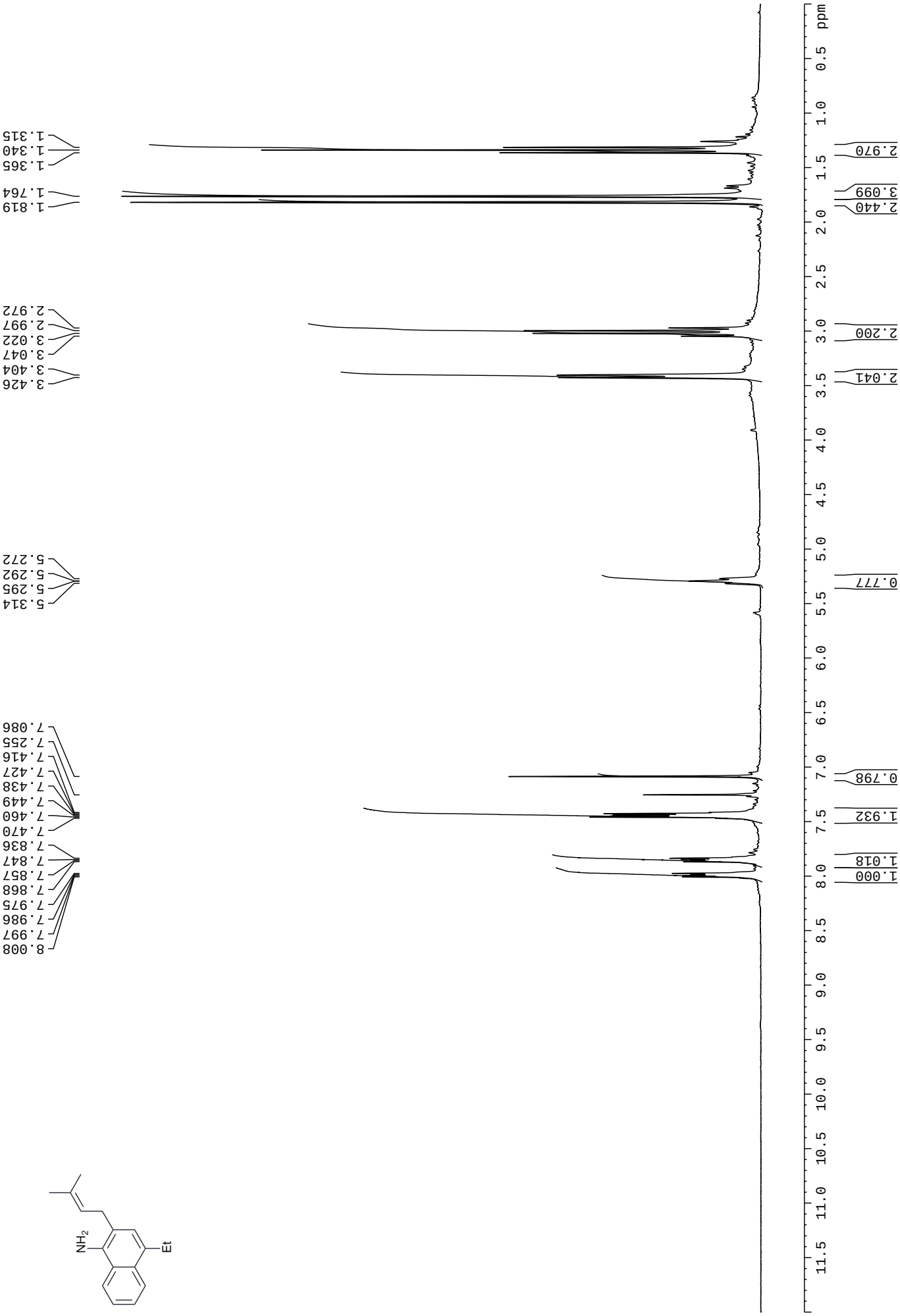
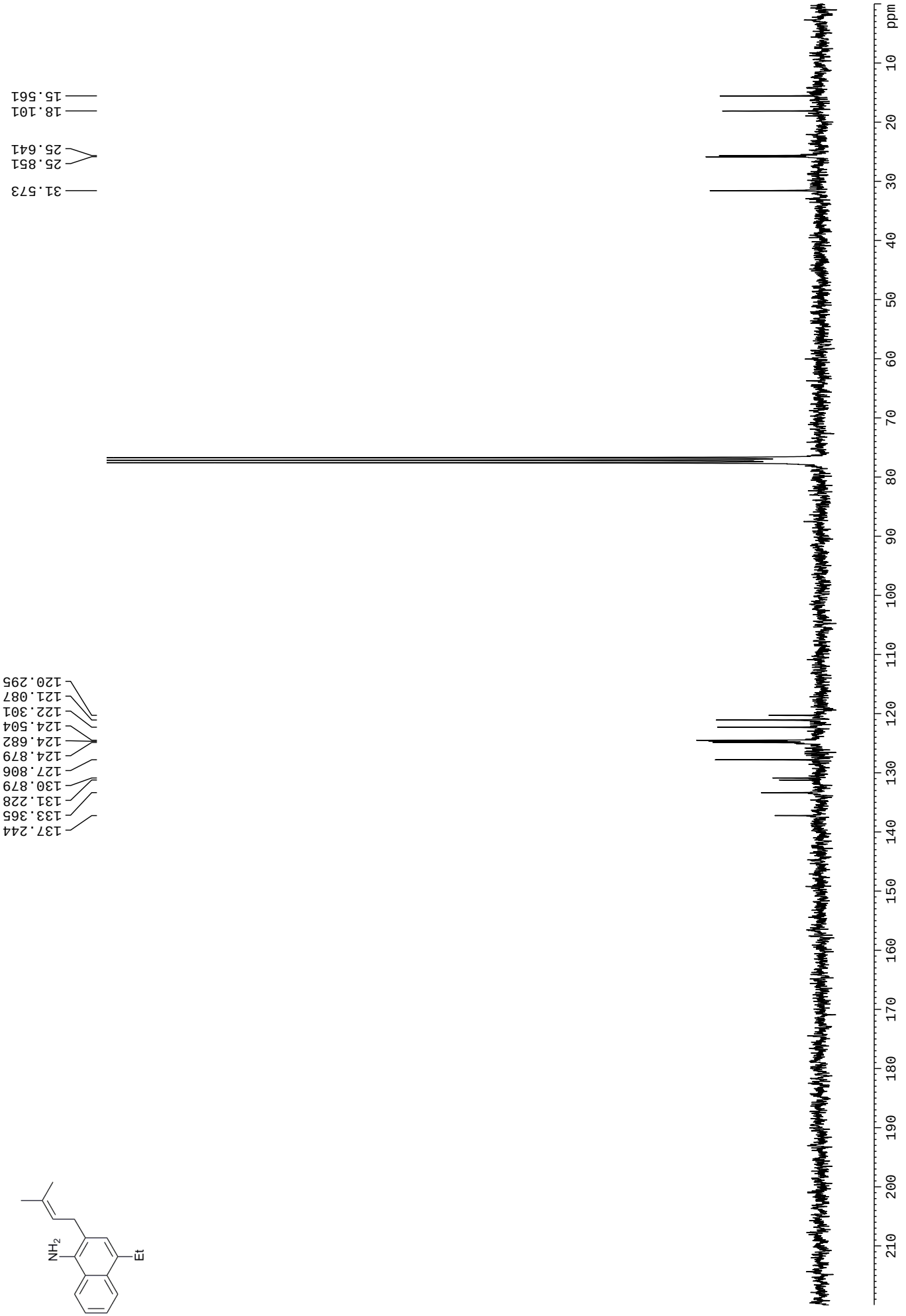
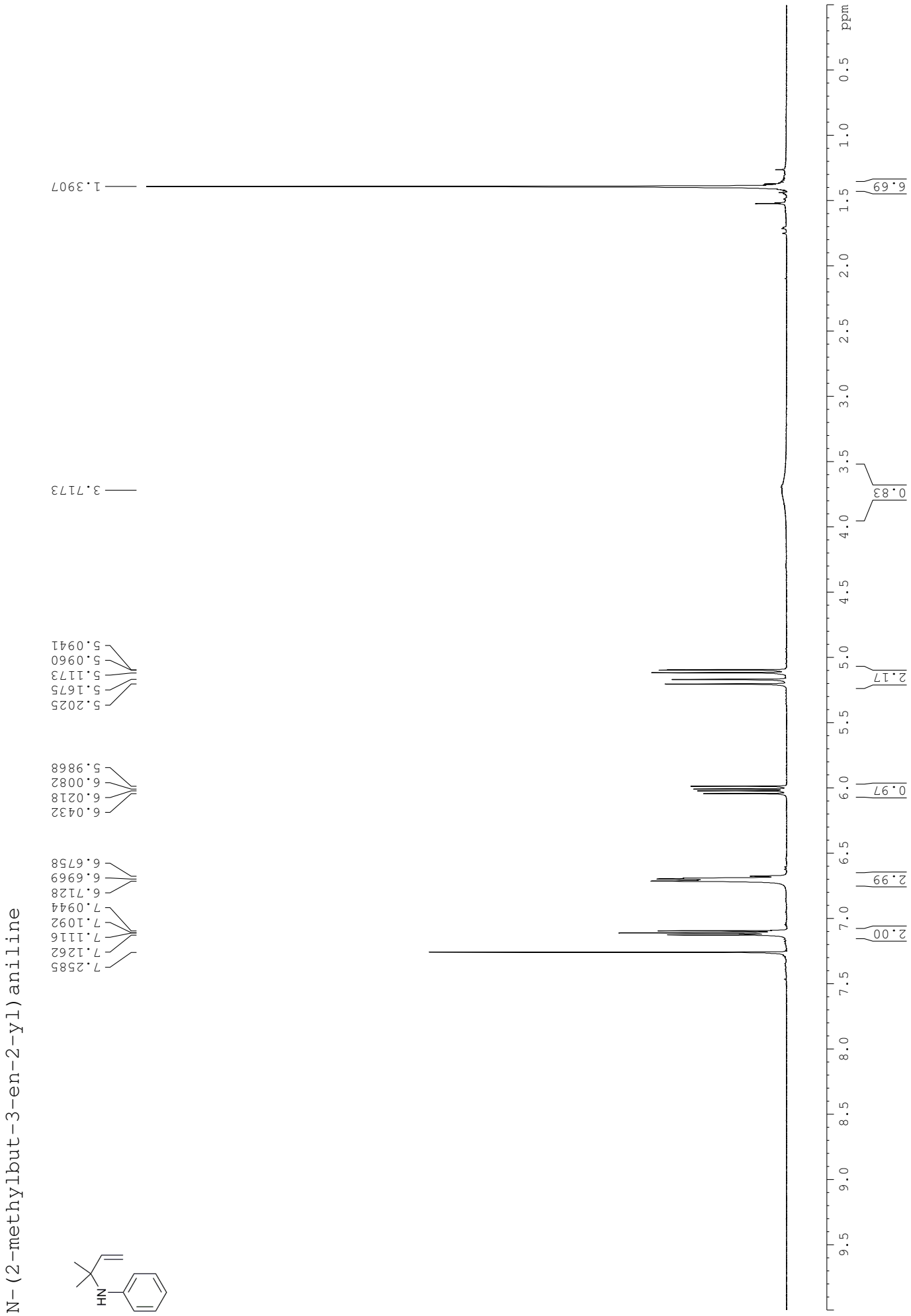
25.72
25.73
31.76
55.88
76.78
77.03
77.28
107.35
120.24
120.34
122.09
122.40
124.36
124.94
125.23
125.69
132.30
133.37
148.68
ppm

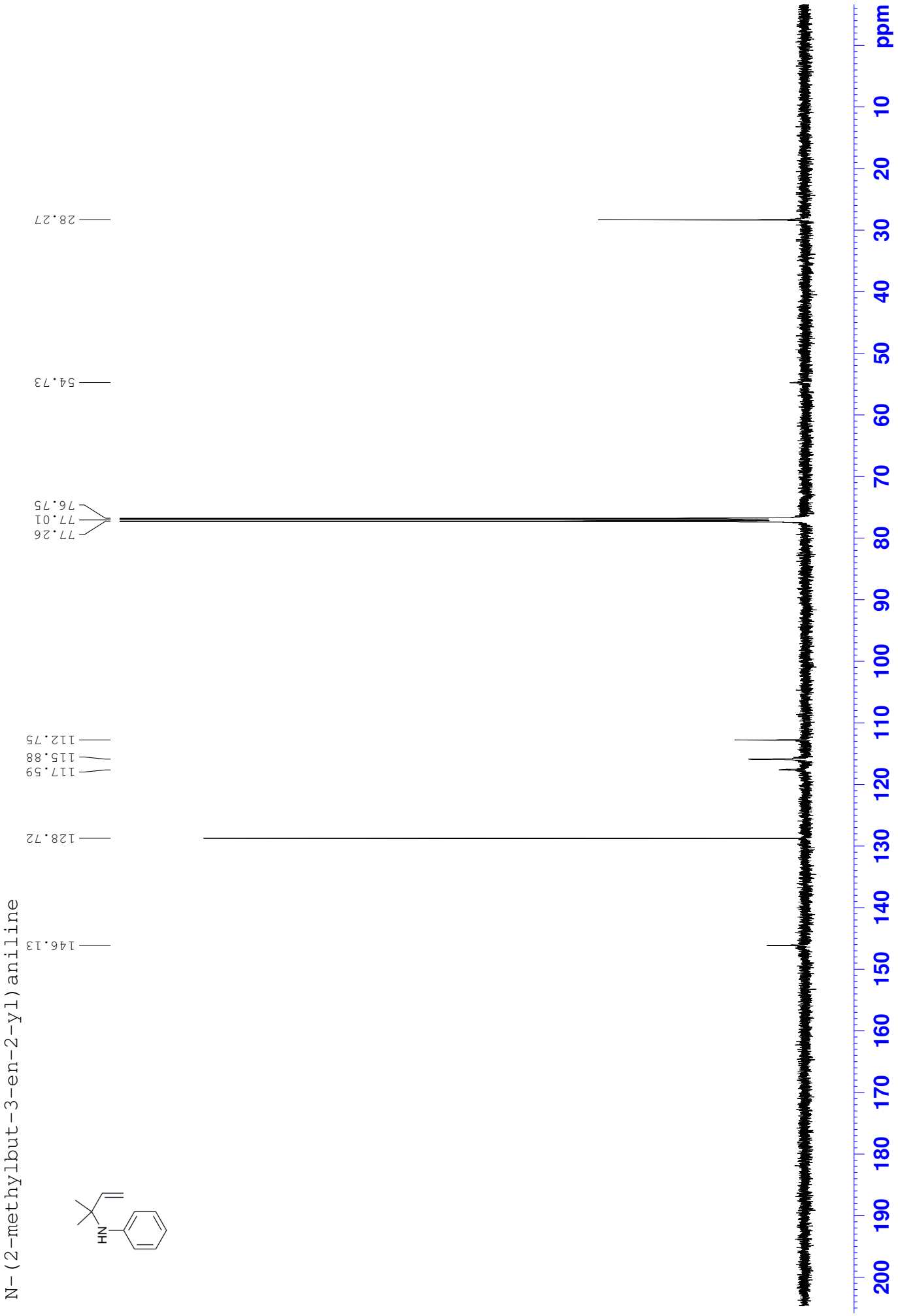


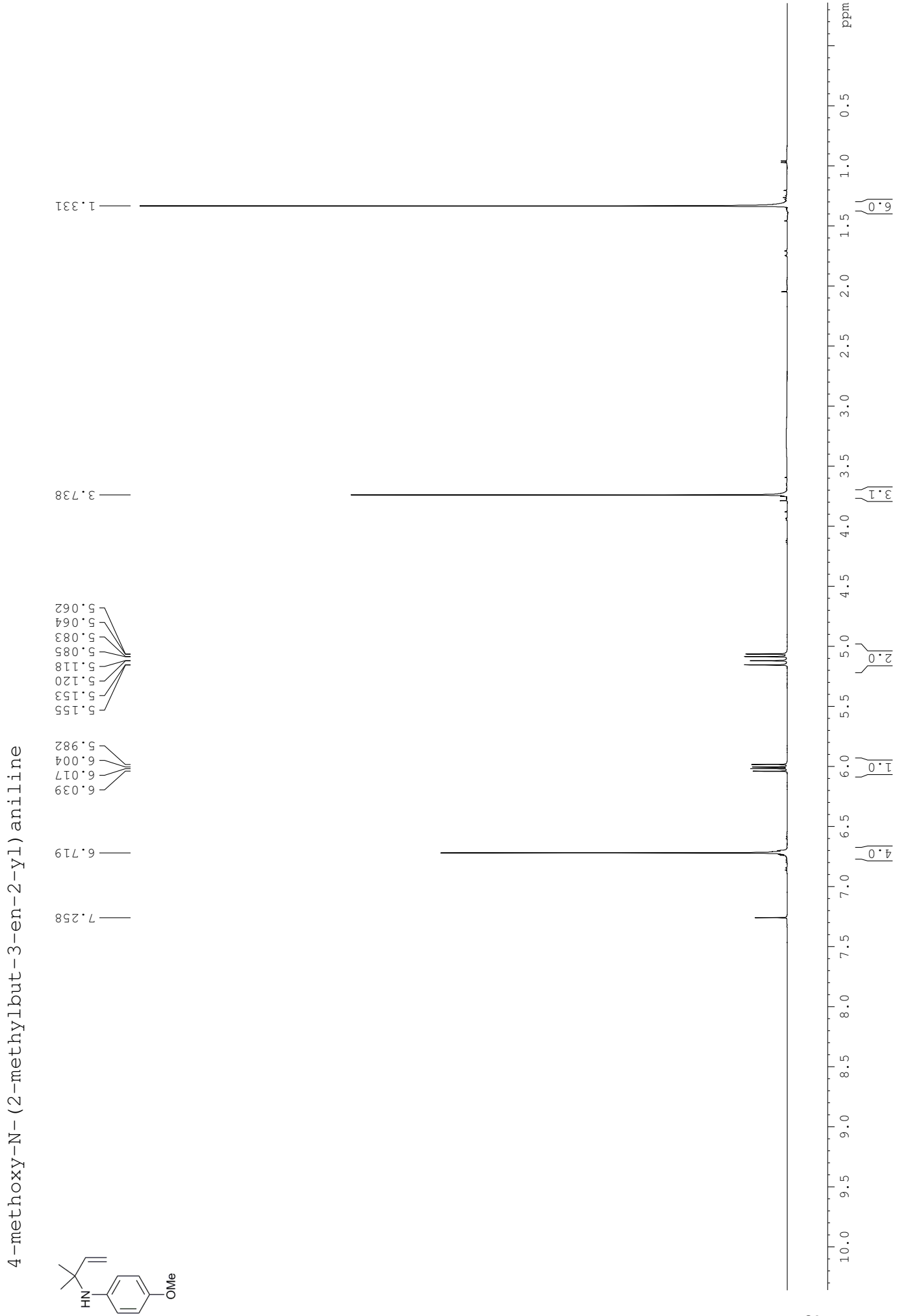


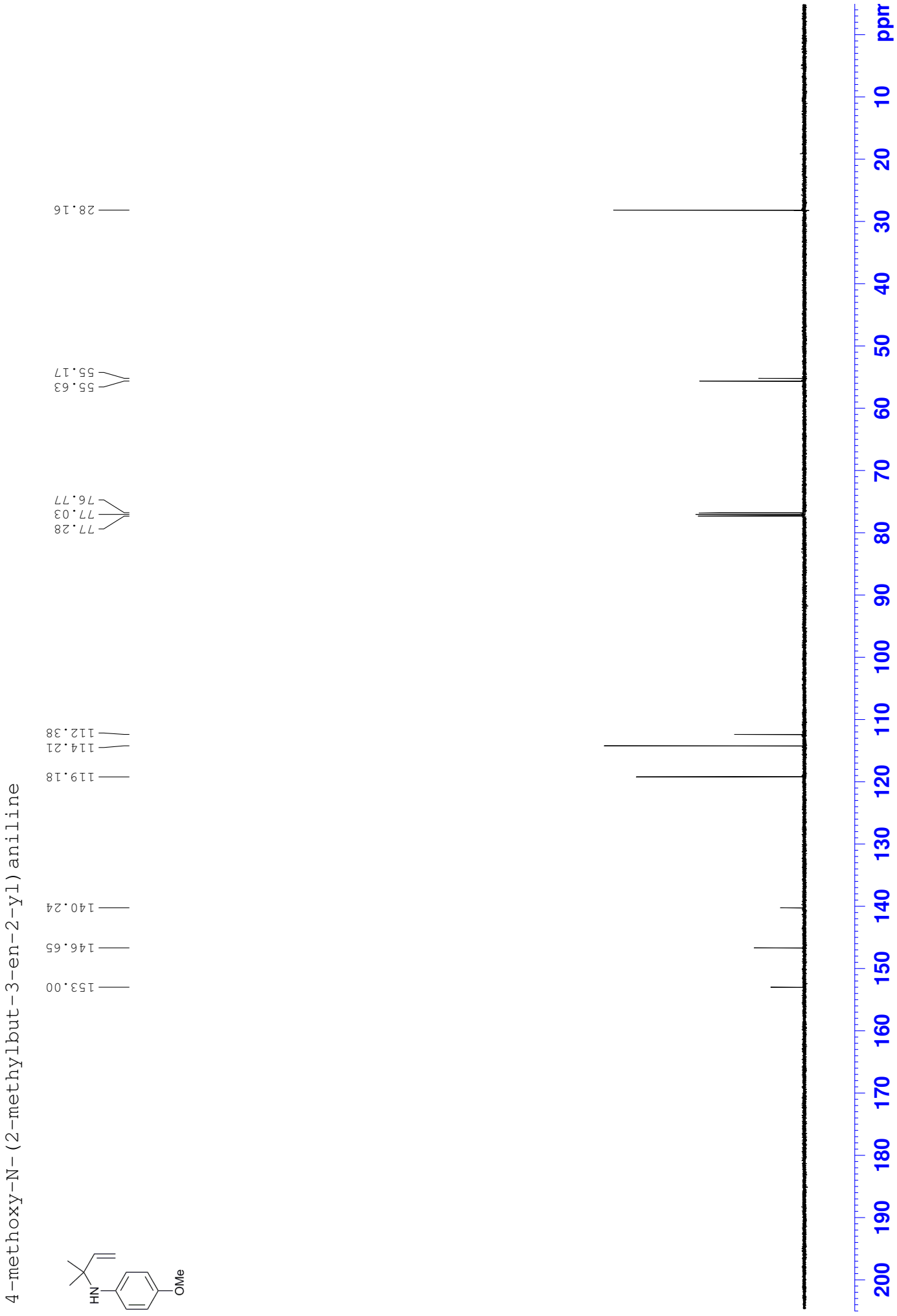


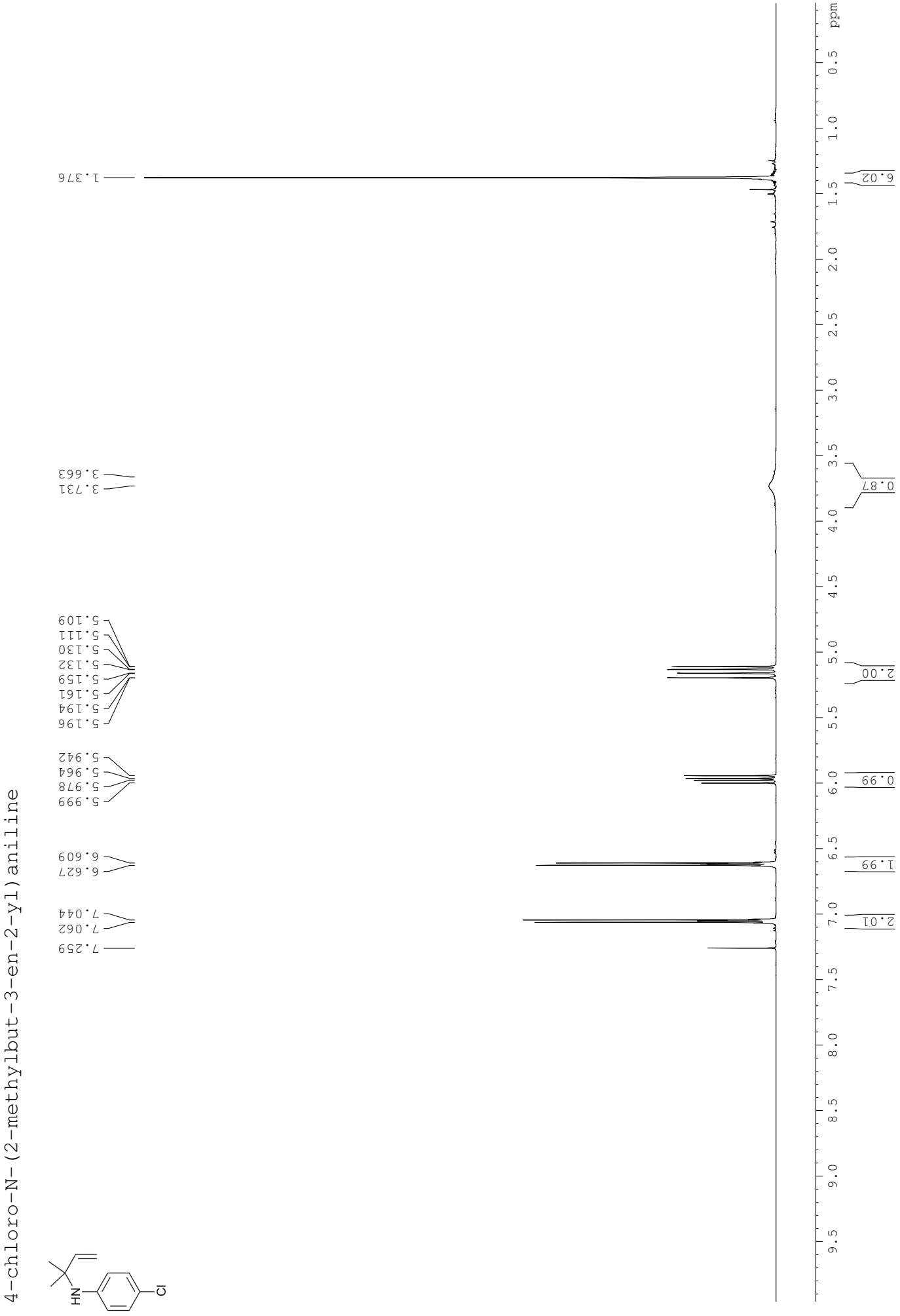


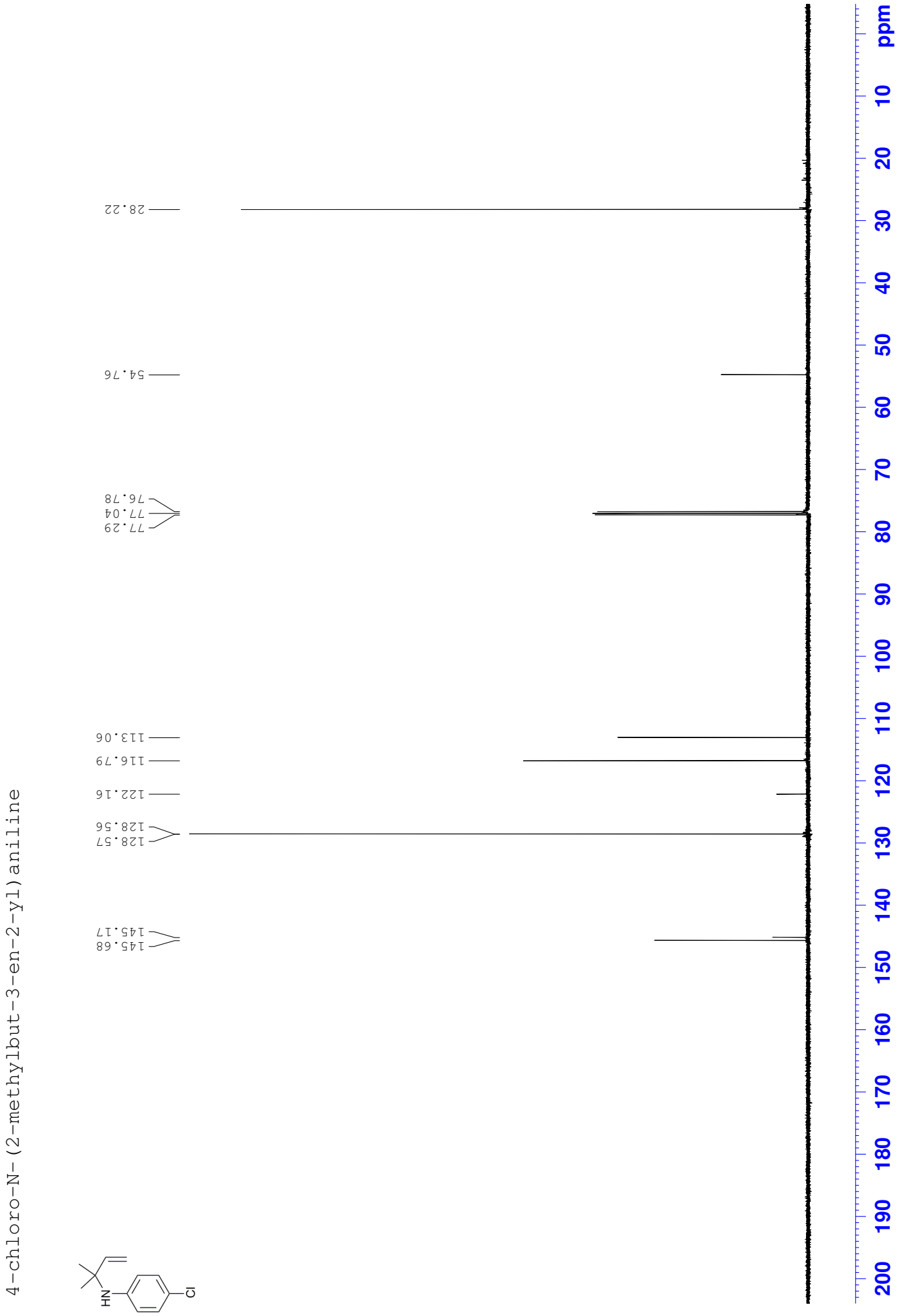







4-methoxy-N-(2-methylbut-3-en-2-yl)aniline
HN
OMe
28.16
55.63
55.17
77.28
77.03
76.77
112.38
114.21
119.18
140.24
146.65
153.00
ppm

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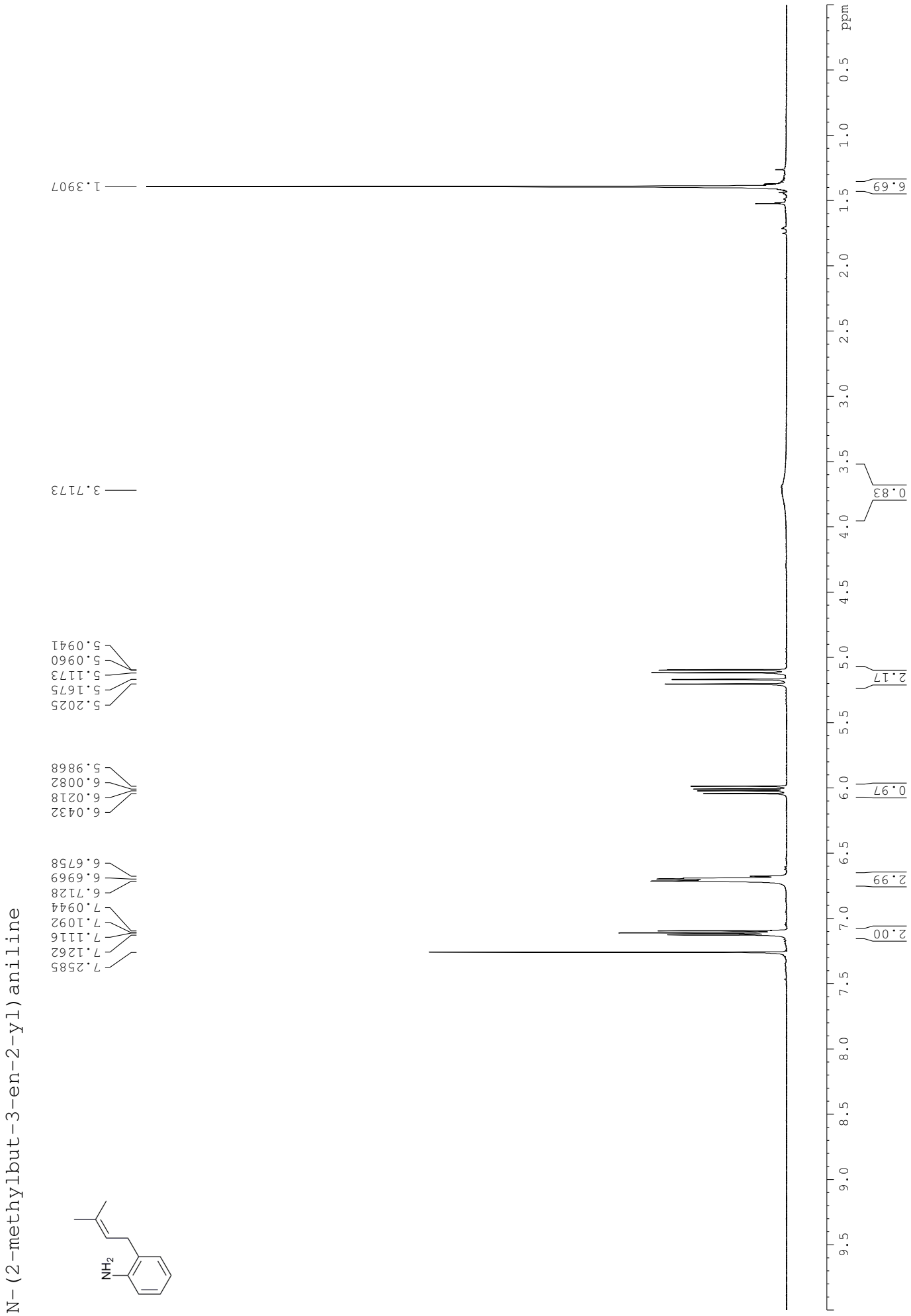
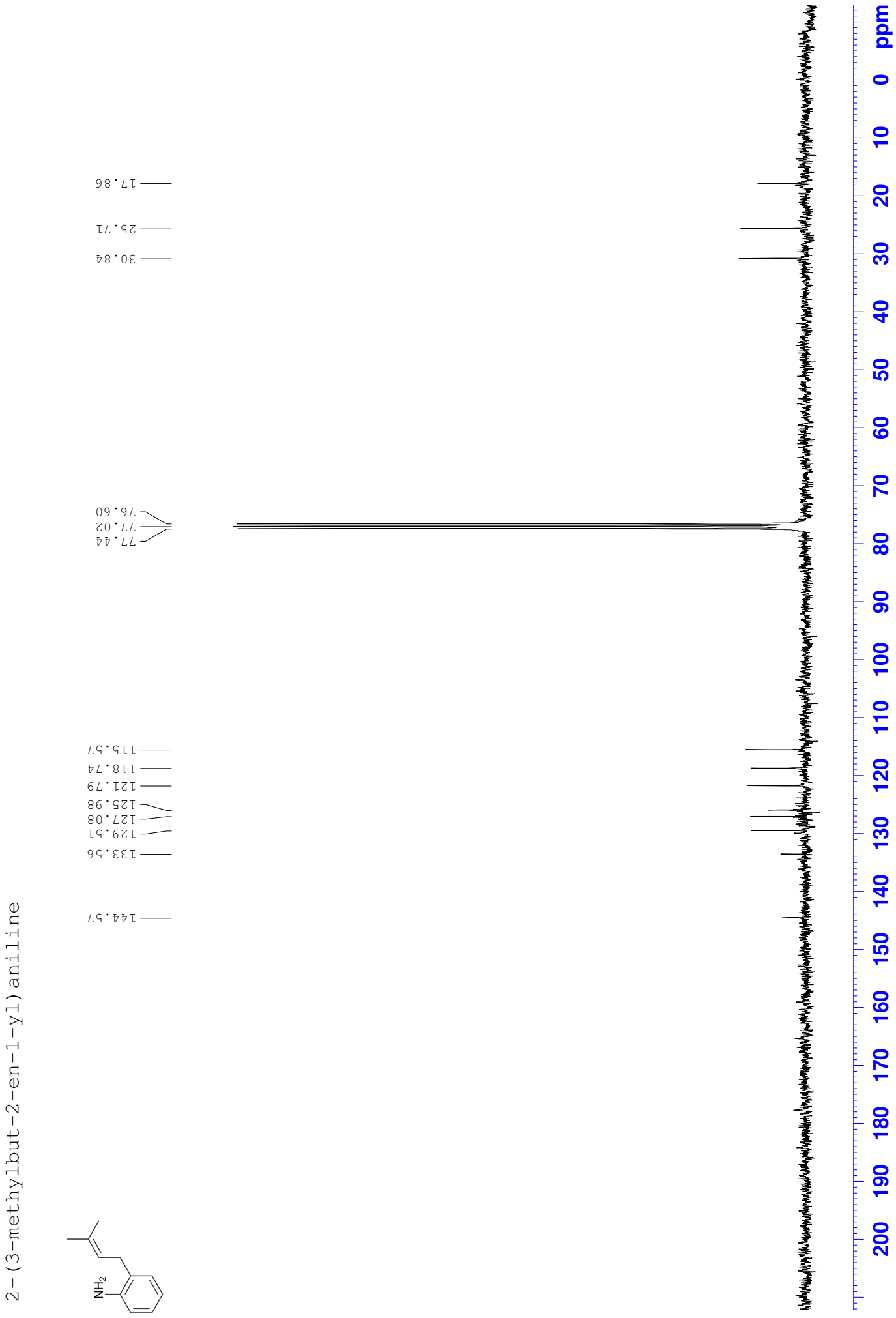
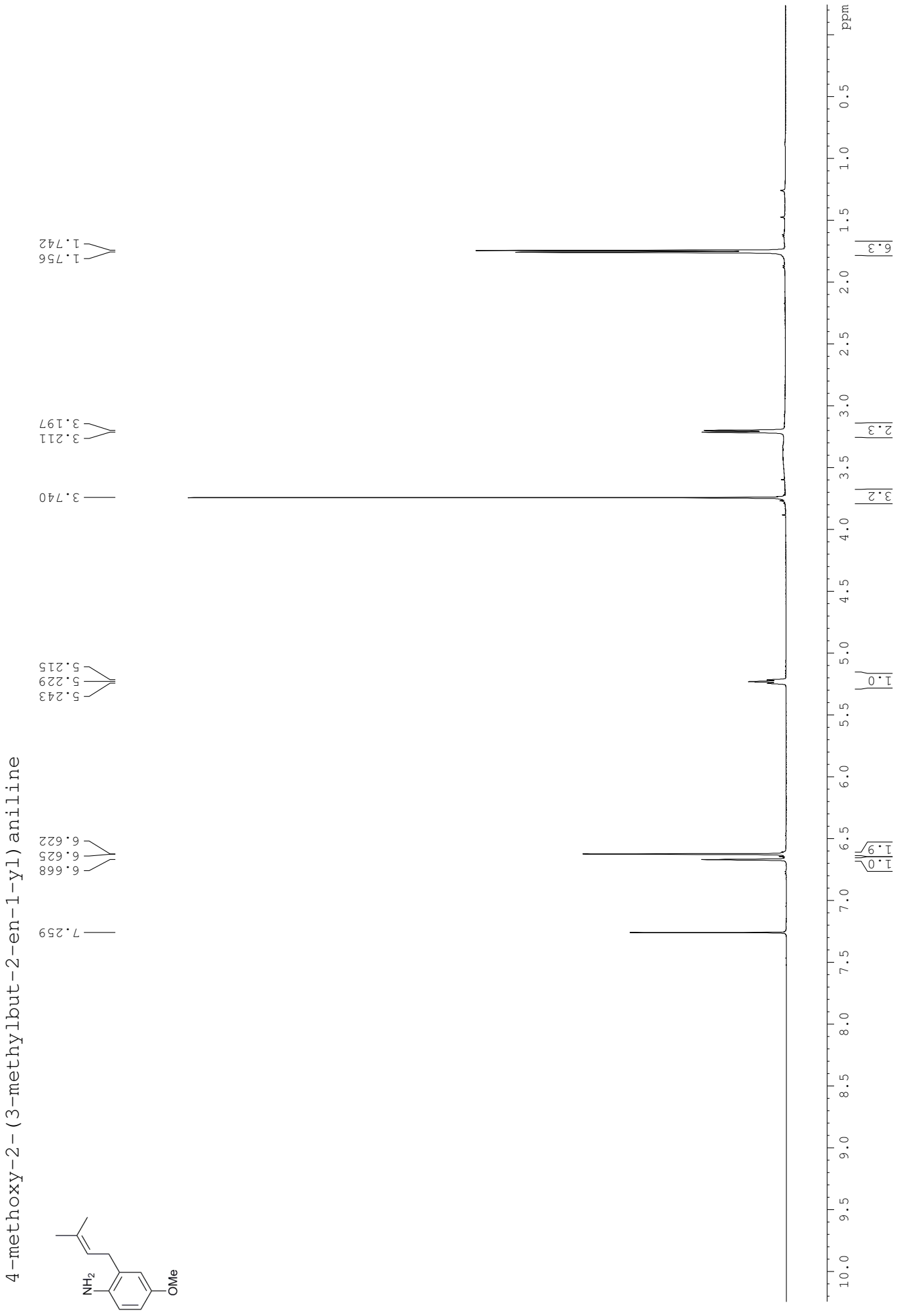
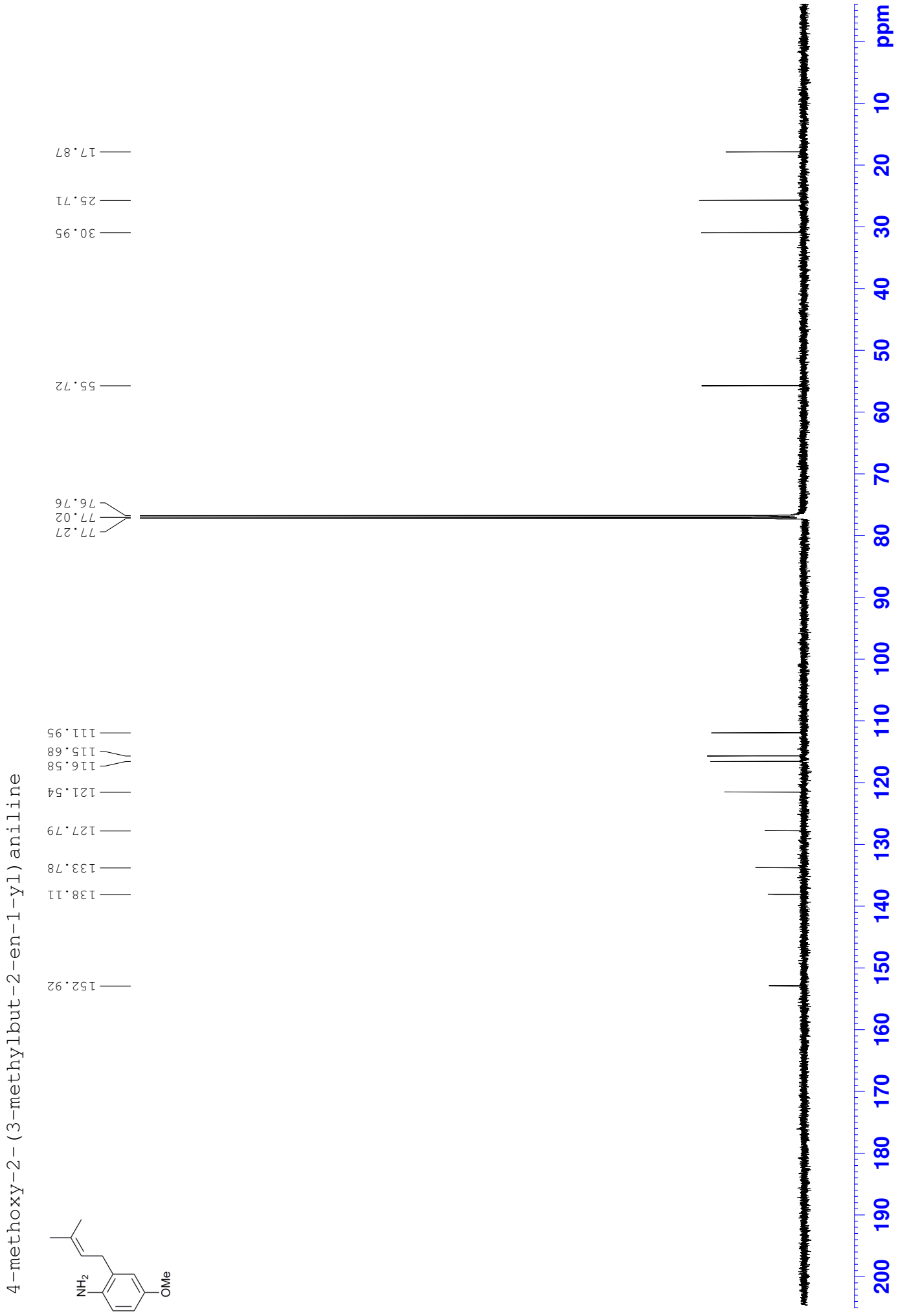
28.22
54.76
76.78
77.04
77.29
113.06
116.79
122.16
128.56
128.57
145.17
145.68
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
NH
Cl

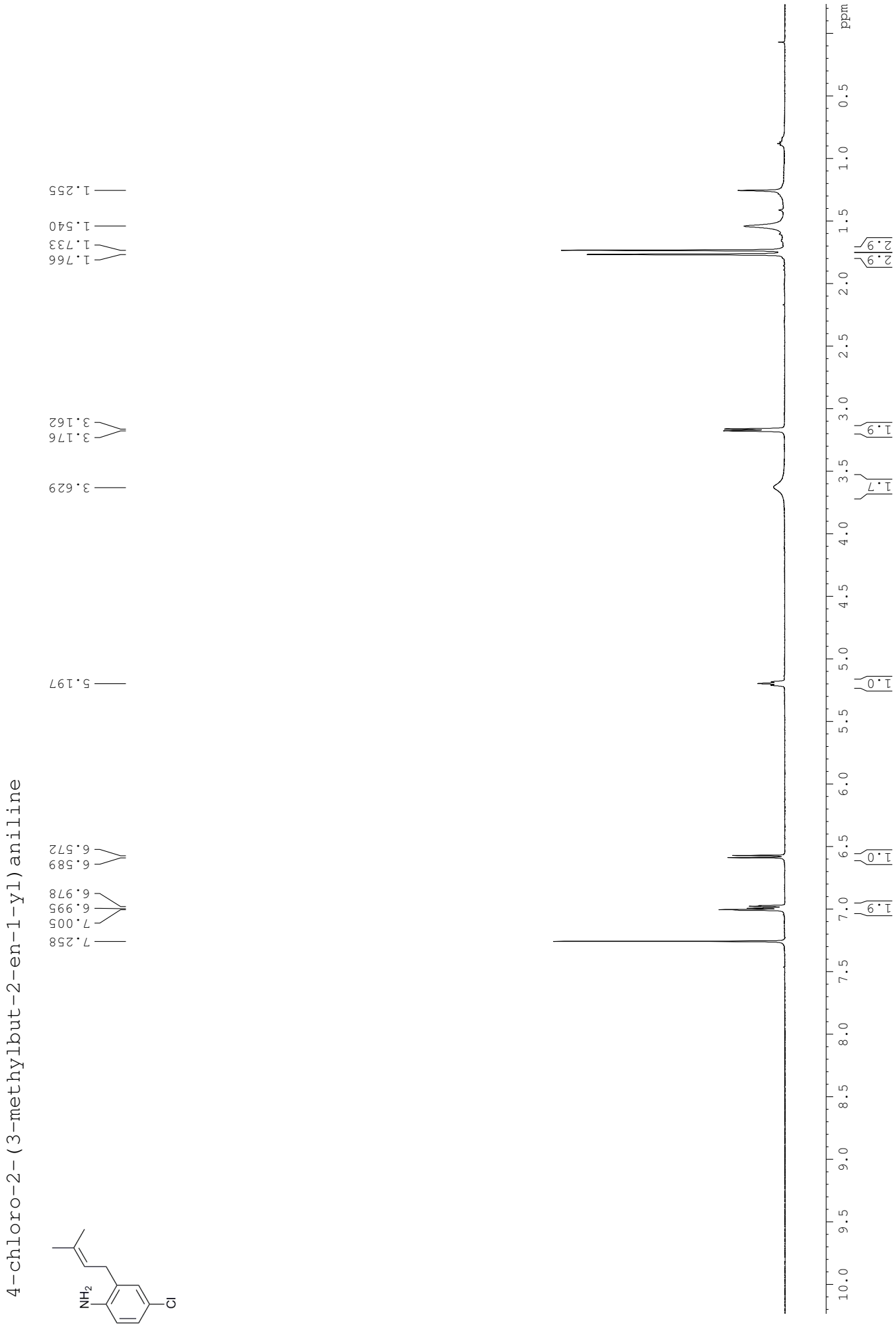


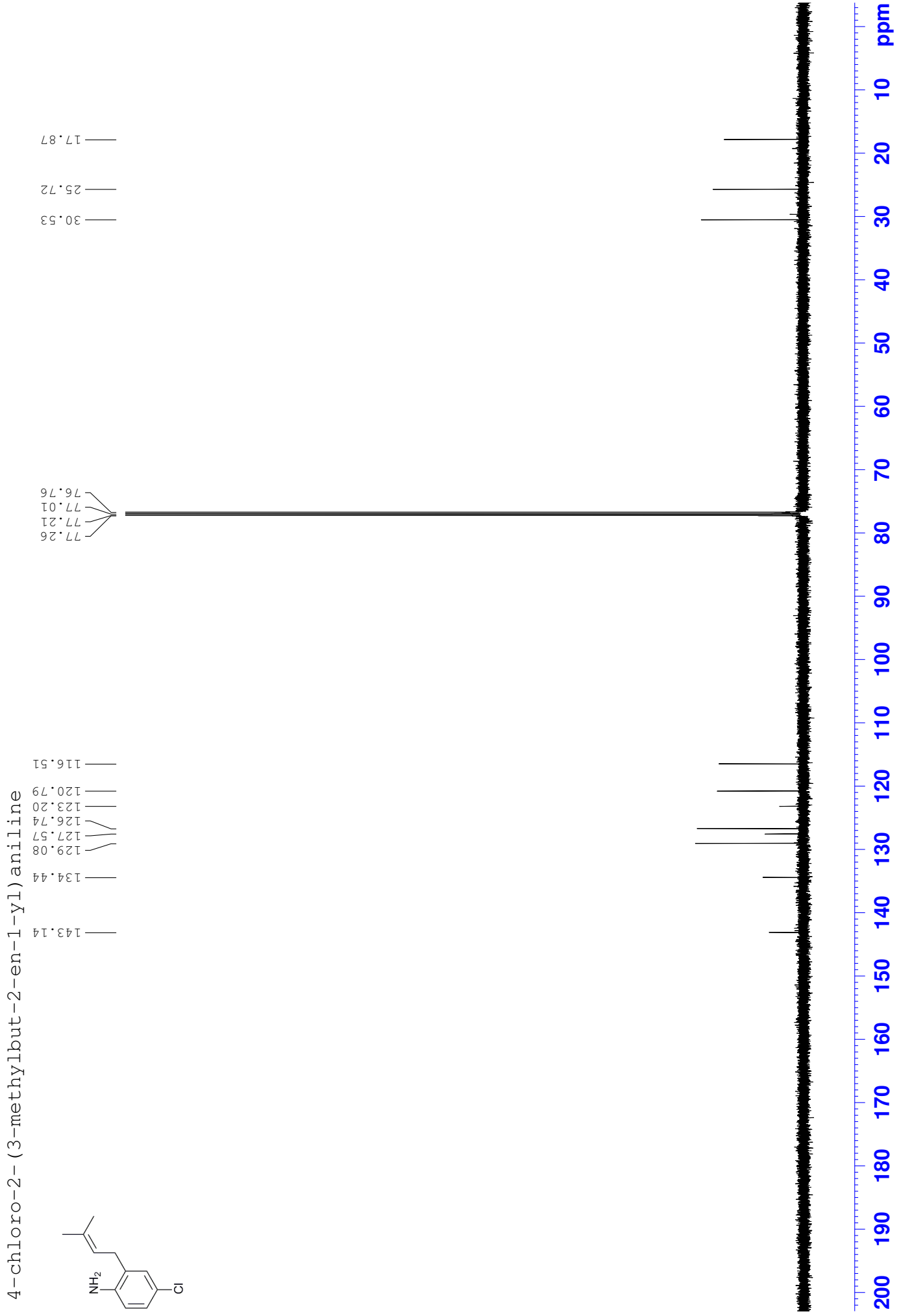


2-(3-methylbut-2-en-1-yl)aniline




4-methoxy-2-(3-methylbut-2-en-1-yl)aniline
NH2
OMe
17.87
25.71
30.95
55.72
76.76
77.02
77.27
111.95
115.68
116.58
121.54
127.79
133.78
138.11
152.92
ppm




4-chloro-2-(3-methylbut-2-en-1-yl)aniline
17.87
25.72
30.53
76.76
77.01
77.21
77.26
116.51
120.79
123.20
126.74
127.57
129.08
134.44
143.14
NH2
Cl
ppm