New J. Chem. Supporting Information

Usual and unusual reactions of cyclohexane-1,2-dione with aryl azides and amines: a structural corrigendum

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[1] General Information

IR spectra were measured on a FT-IR Spectrometer *Nicolet iS5* from THERMO FISCHER SCIENTIFIC. Spectra were measured in suitable organic solvents and are reported in cm^{-1} in decreasing order of wavenumber ($\tilde{\nu}$).

NMR spectra were measured on *a UNITY INOVA 400* FT spectrometer from VARIAN. ^{1}H NMR spectra were measured at 400 MHz and ^{13}C NMR at 100 MHz. NMR signals were referenced to TMS (δ = 0) or solvent signals and recalculated relative to TMS. 2D NMR methods, such as gCOSY gHSQCAD, CIGAR etc. were used for assignment of signals, when necessary. Multiplicities of the signals are reported using the standard notations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. s = broad singlet, etc.

Mass spectra were obtained from *micrOTOF QII* spectrometer from BRUKER utilizing electrospray-ionisation technique (ESI).

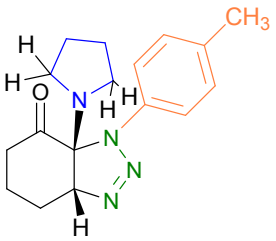
Quantitative elemental analyses were performed on a *Vario Micro Tube* from ELEMENTAR ANALYSENSYSTEME GMBH HANAU.

Thin layer chromatography was performed using *Macherey-Nagel Polygram SIL G/UV$_{254}$ foils*.

Flash chromatography was performed with Silica gel 60 M (particle-size 0.04−0.063 mm) as the stationary phase from the company *Macherey-Nagel*.

Melting points were recorded on a *Pentakon Dresden Boetius* apparatus and are uncorrected.

[2] Synthesis and characterisation of triazole 3e:

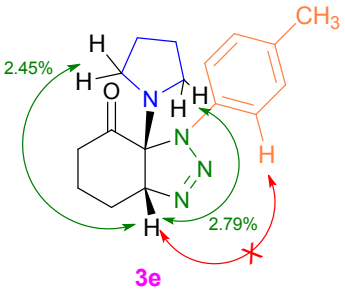


3e

General Procedure: To a solution of cyclohexane-1,2-dione (0.3 mmol) and the corresponding aryl azide (0.6 mmol) in THF (1.0 mL), was added pyrrolidine (0.3 mmol) and the mixture was stirred for 48 h at RT. Purification by silica-gel flash chromatography yields the desired products **3b** and **3e**.

Supposed product **1e** from cyclohexane-1,2-dione, pyrrolidine and 1-azido-4-methylbenzene	Product **3e** from cyclohexane-1,2-dione, pyrrolidine and 1-azido-4-methylbenzene
Yellow oil; yield (76%).	Yellow oil; yield (47%); purified by flash chromatography (R_f = 0.45; SiO_2; Et_2O:*n*-pentane 1:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.45–1.50 (m, 1H), 1.63–1.76 (m, 6H), 2.19–2.32 (m, 6H), 2.40–2.44 (m, 2H), 2.61–2.64 (m, 2H), 4.81–4.83 (m, 1H), 7.09 (d, *J* = 10 Hz, 2H), 7.39 (d, *J* = 10 Hz, 2H).	**^{1}H NMR (400 MHz, $CDCl_3$):** δ = 1.41–1.53 (m, 1H), 1.59–1.79 (m, 6H), 2.18–2.37 (m, 3H), 2.28 (s, 3H), 2.39–2.44 (m, 2H), 2.61–2.66 (m, 2H), 4.81 (m, 1H), 7-08 (d, ^3J = 8.8 Hz), 7.39 (d, ^3J = 8.8 Hz, 2H).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.1, 20.7, 24.0, 26.3, 37.3, 45.8, 81.0, 82.9, 116.7, 129.7, 133.6, 137.2, 204.2	**^{13}C NMR (100 MHz, $CDCl_3$):** δ = 17.07 (t, $CHCH_2$), 20.68 (q, CH_3), 23.94 (t, NCH_2CH_2, 2 x CH_2), 26.27 (t, $COCH_2CH_2$), 37.26 (t, $COCH_2$), 45.71 (t, NCH_2, 2 x CH_2), 80.95 (d, CH), 82.82 (s, NCN), 116.66 (d, *C*–2'), 129.69 (d, *C*–3'), 133.54 (s, C_{quat}), 137.16 (s, C_{quat}), 204.15 (s, *C*=O).
IR: N.A.	**IR ($CDCl_3$, cm^{-1}):** 1722 (C=O).
HR-MS (ESI): m/z calcd. for $C_{17}H_{23}N_4O_2$ $[M]^+$ 299.1866; found: 299.1863	**HR-MS (ESI):** m/z calcd. for $C_{17}H_{24}N_4O_2$ $[M + H]^+$ 299.1866; found: 299.1849

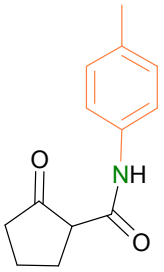
The structure assignment for **3e** has been further confirmed by 1D NOESY and gHSQCAD NMR analytical techniques.



3e

Scheme 1. Results from the 1D NOESY experiment (**3e**).

[3] Synthesis and characterisation of amide 4e:



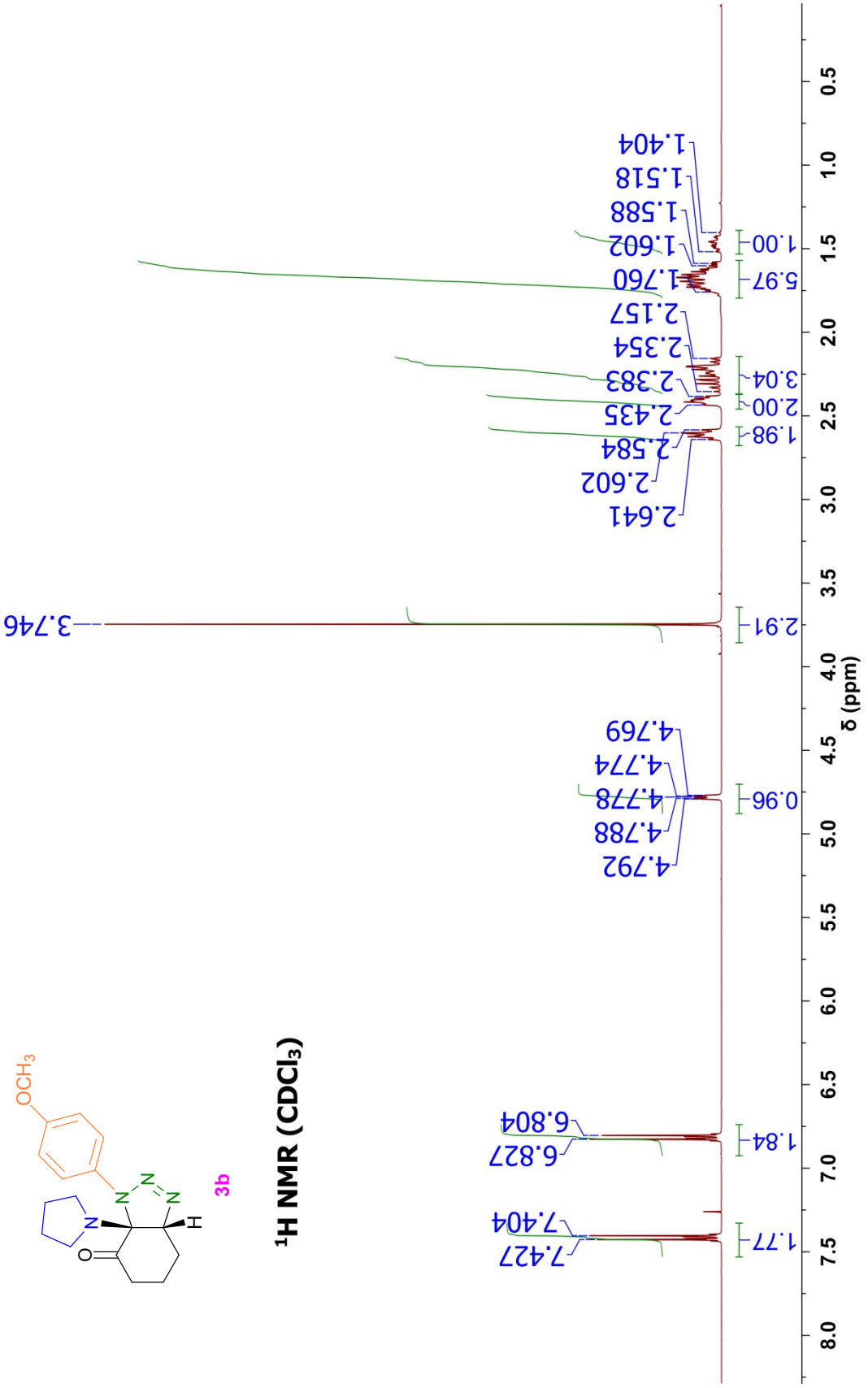
4e

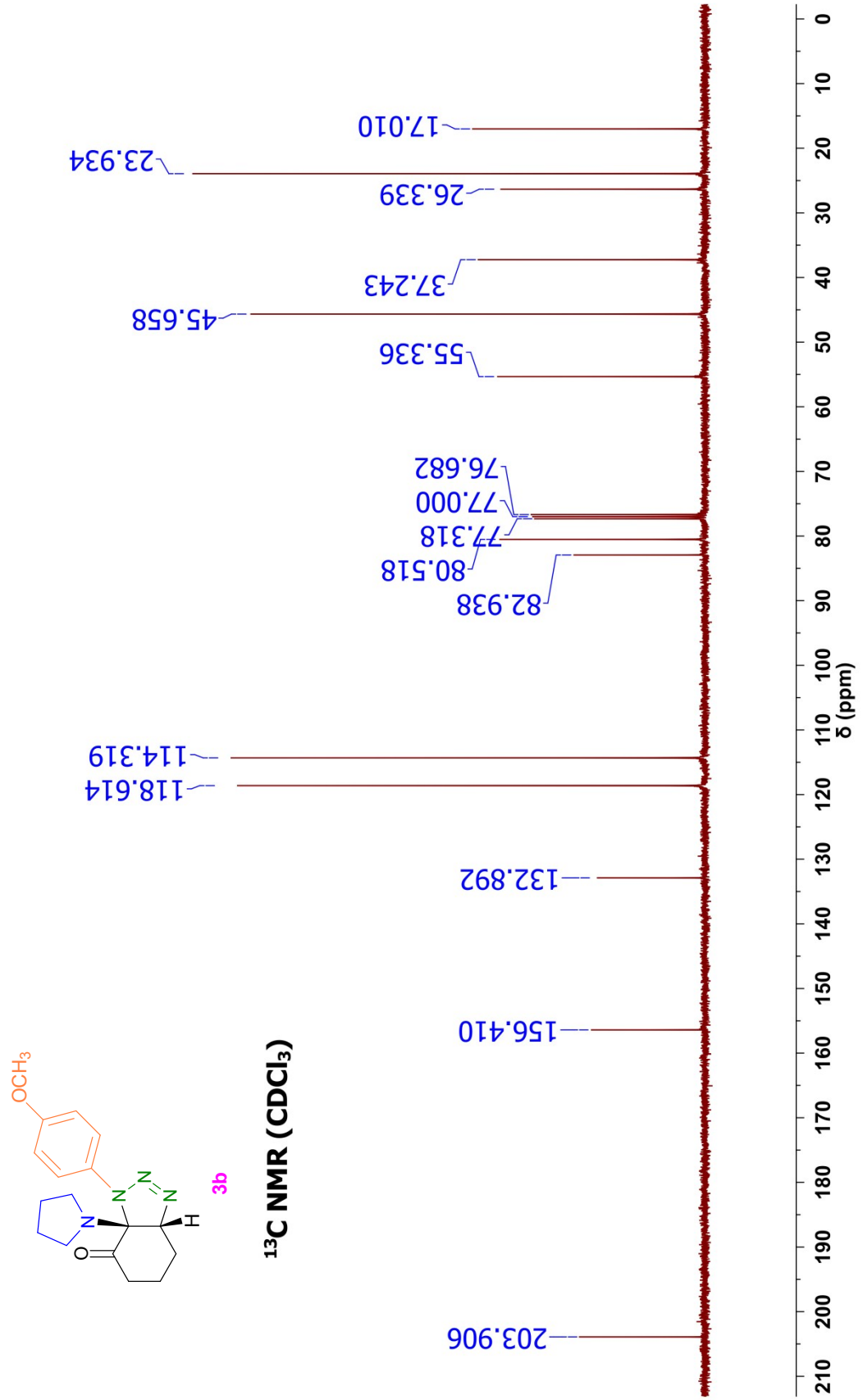
General Procedure: To a solution of cyclohexane-1,2-dione (0.3 mmol) and the corresponding aryl azide (1.2 mmol) in $CHCl_3$ (1.1 mL), was added diethylamine (0.3 mmol) and the mixture was stirred for 48 h at RT. Purification by silica-gel flash chromatography yields the desired products **4b** and **4e**.

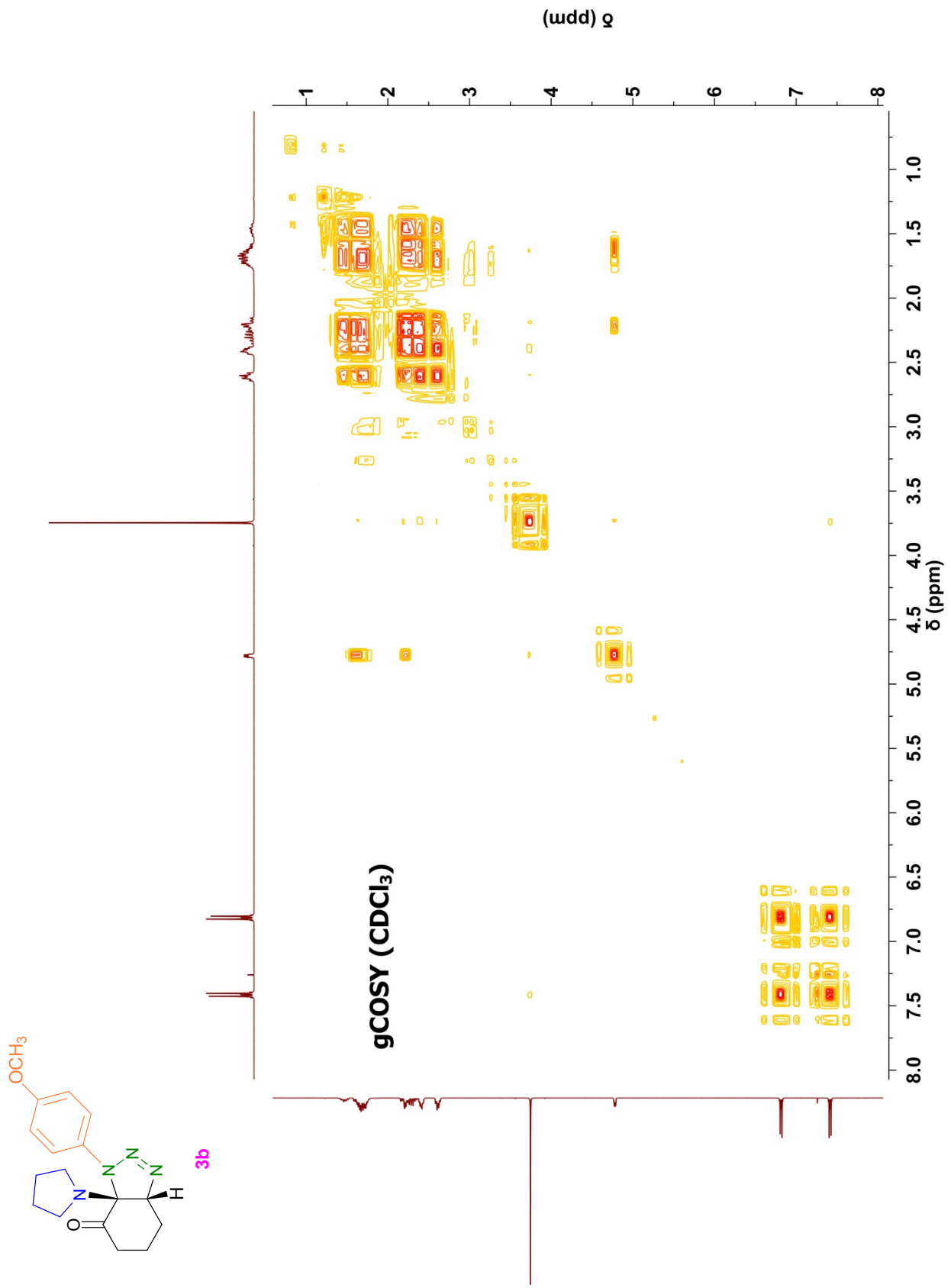
Supposed product **2e**[8a] from cyclohexane-1,2-dione, diethylamine and 1-azido-4-methylbenzene	Product **4e** from cyclohexane-1,2-dione, diethylamine and 1-azido-4-methylbenzene
Yellow solid. mp N.A.	Yellow solid; yield (53%); mp 127 °C; purified by flash chromatography (R_f = 0.42; SiO_2 : Et_2O).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.83–1.91 (m, 1H), 2.06–2.11 (m, 1H), 2.30 (s, 3H), 2.32–2.47 (m, 4H), 3.13 (t, J = 10 Hz, 1H), 7.11 (d, J = 10 Hz, 2H), 7.42 (d, J = 10 Hz, 2H), 8.65 (br., 1H).	**^{1}H NMR (400 MHz, $CDCl_3$):** δ = 1.77–1.89 (m, 1H), 1.99–2.14 (m, 1H), 2.26–2.46 (m, 4H), 2.30 (s, 3H), 3.12 (t, ^3J = 9.2 Hz), 7.10 (d, ^3J = 8.4 Hz, 2H), 7.41 (d, ^3J = 8.4 Hz), 8.70 (br. s, 1H, NH).
^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.2, 20.8, 25.7, 39.1, 54.6, 119.9, 129.4, 133.9, 135.1, 164.3, 217.0	**^{13}C NMR (100 MHz, $CDCl_3$):** δ = 20.14 (t, CH_2), 20.78 (q, CH_3), 25.67 (t, CH_2), 38.98 (t, CH_2), 54.58 (d, CH), 119.75 (d, C–2' or C–3'), 129.33 (d, C–2' or C–3'), 133.75 (s, C_{quat}), 135.07 (s, C_{quat}), 164.41 (s, $CONH$), 216.87 (C=O).
Anal. calcd. for N.A.	**Anal. calcd. for** $C_{13}H_{15}NO_2$: C 71.87, H 6.96, N 6.45; found: C 70.99, H 7.04, N 6.27
IR: N.A.	**IR ($CHCl_3$, cm^{-1}):** 1728 (C=O), 1681 (CONH), 3341 (NH).
HR-MS (ESI): m/z calcd. for $C_{13}H_{16}N_3O_2$ $[M]^+$ 246.1243; found: 246.1246	**HR-MS (ESI):** m/z calcd. for $C_{13}H_{16}NO_2$ $[M + H]^+$ 218.1176; found: 218.1149; for $C_{13}H_{15}NNaO_2$ $[M + Na]^+$ 240.0995; found: 240.0970

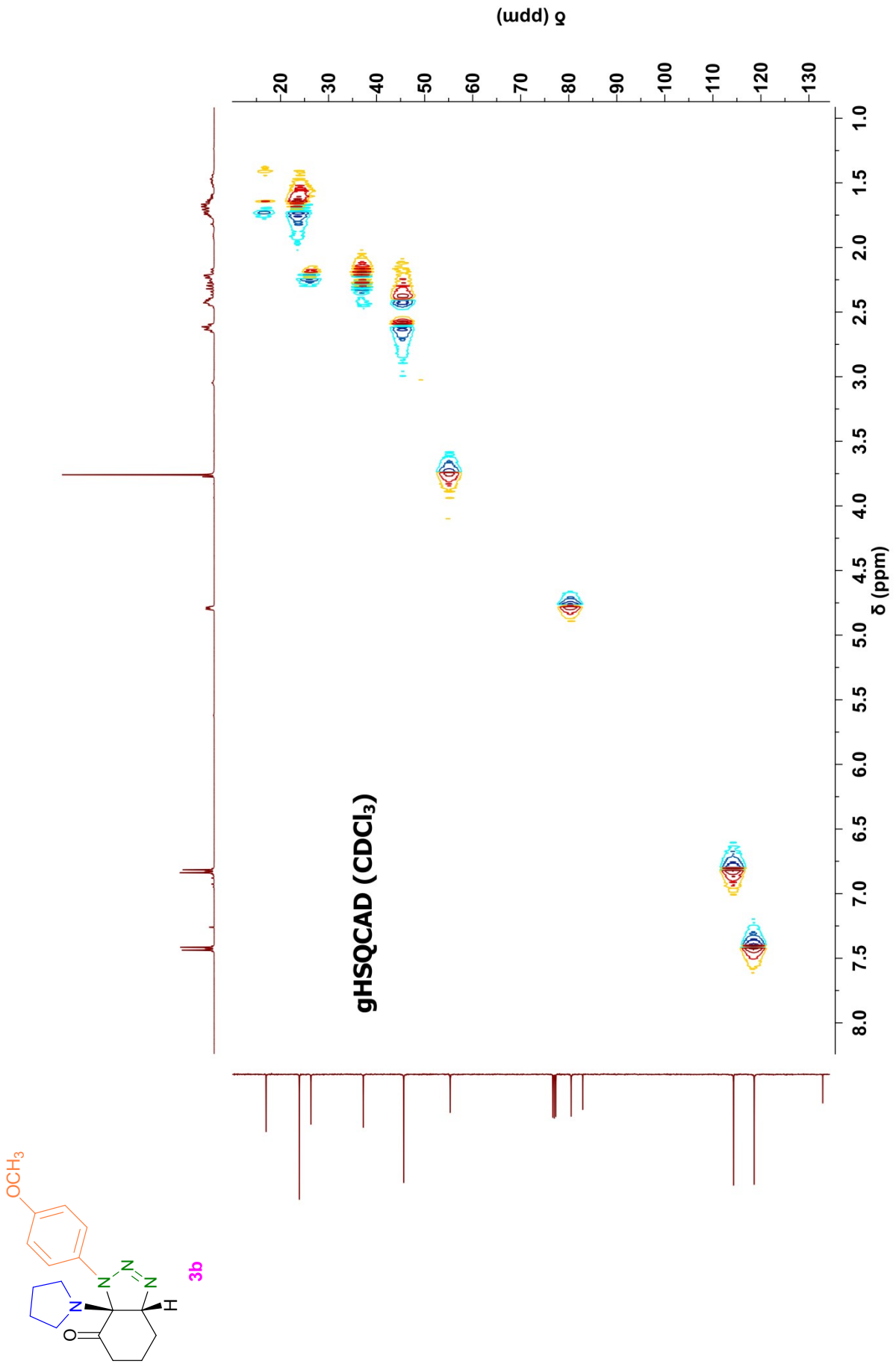
Note: *This molecule was also prepared by a known analogous method[15b] for comparision. The spectra (pages 25–26) match perfectly with the above data.*

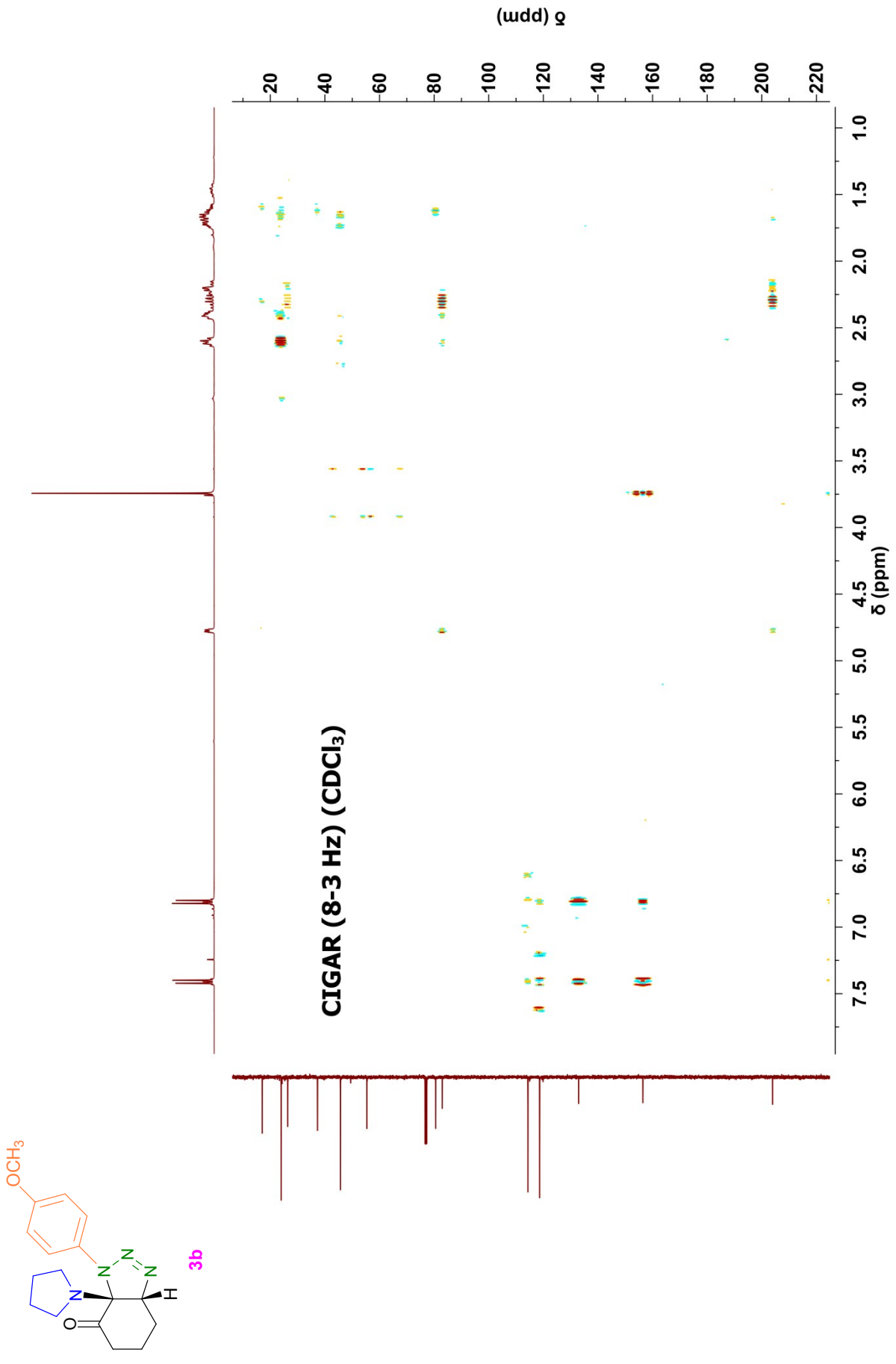
[4] NMR and IR spectra

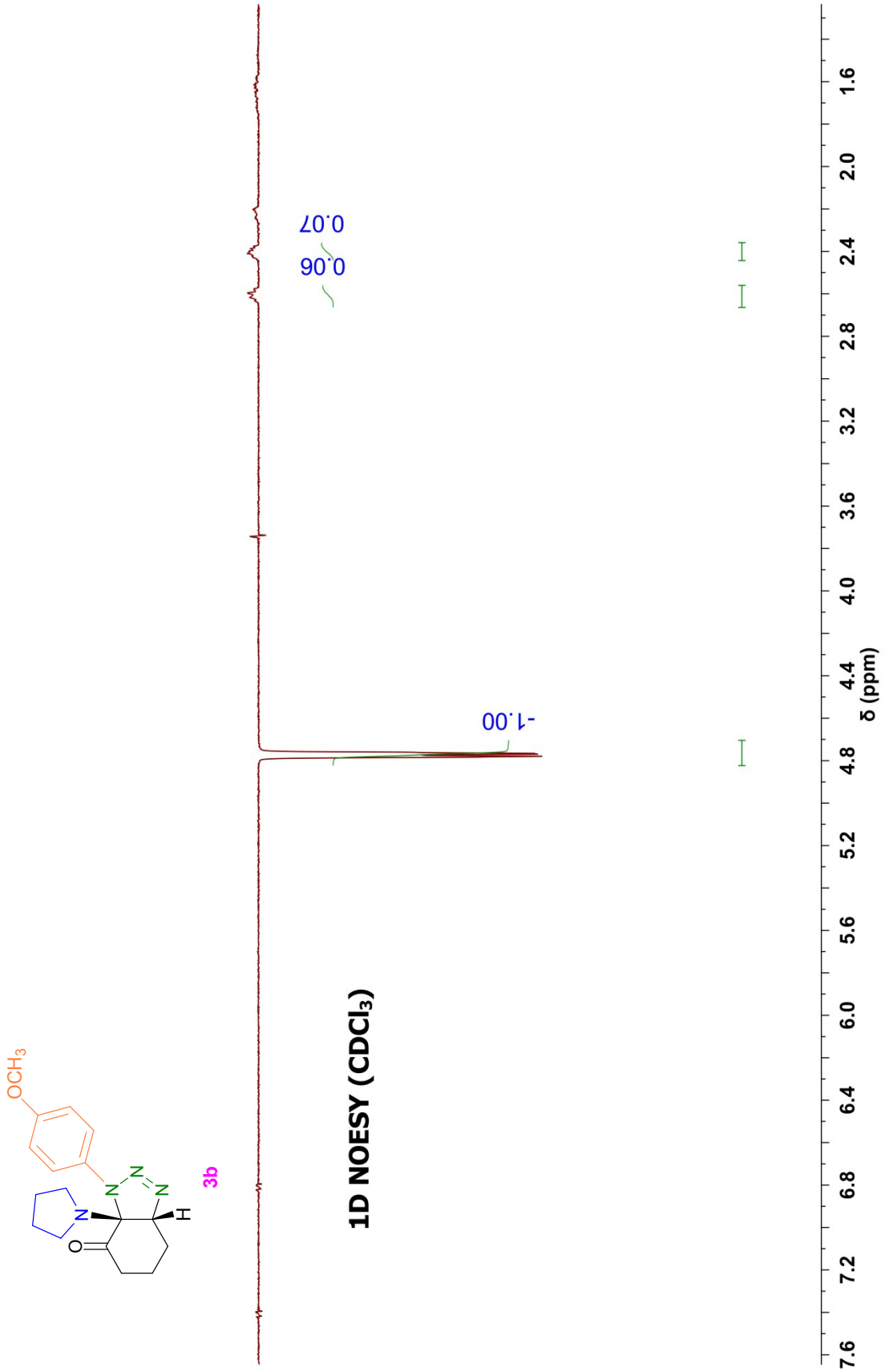


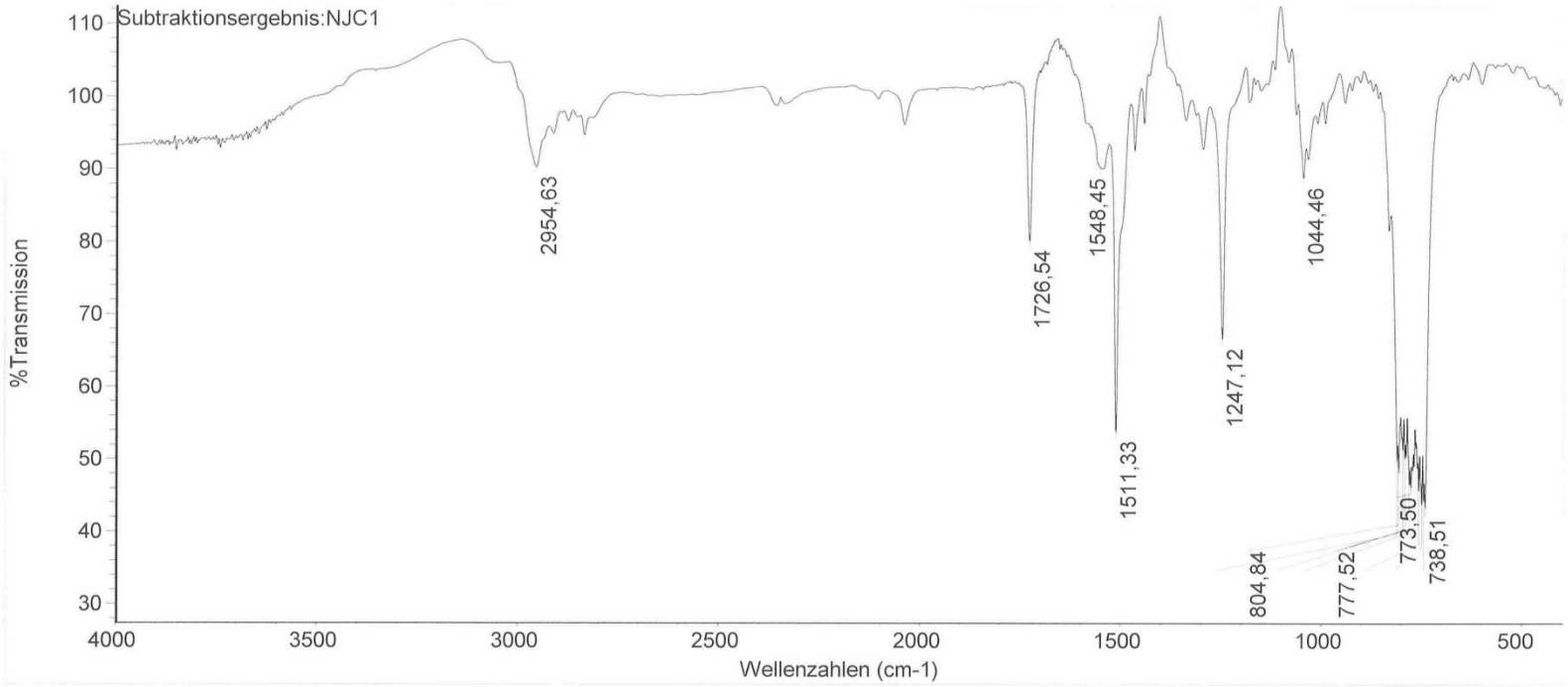

203.906
156.410
132.892
118.614
114.319
82.938
80.518
77.318
77.000
76.682
55.336
45.658
37.243
26.339
23.934
17.010
δ (ppm)
^{13}C NMR (CDCl$_3$)
3b
OCH$_3$


gCOSY (CDCl3)
δ (ppm)
δ (ppm)
OCH3
3b


gHSQCAD (CDCl3)
δ (ppm)
δ (ppm)
OCH3
3b


CIGAR (8-3 Hz) (CDCl3)
δ (ppm)
δ (ppm)
OCH3
3b


1D NOESY ($CDCl_3$)
3b
OCH_3
-1.00
0.06
0.07
δ (ppm)



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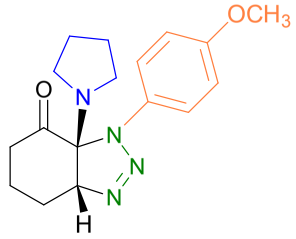
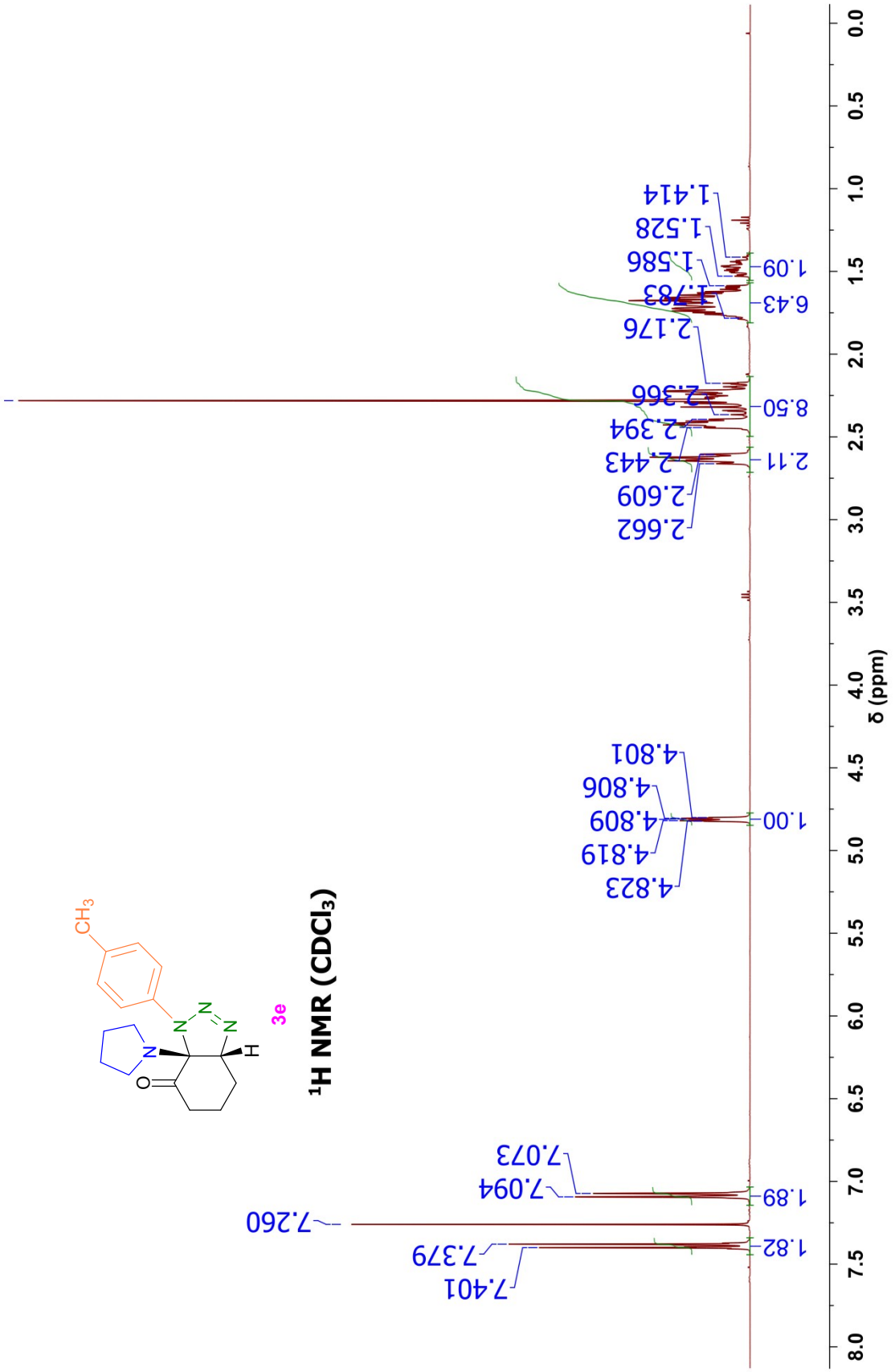


3b


^{1}H NMR ($CDCl_3$)
3e
CH_3
N
N
N
H
O
7.401
7.379
7.260
7.094
7.073
1.89
1.82
4.823
4.819
4.809
4.806
4.801
1.00
2.662
2.609
2.443
2.394
2.366
8.50
2.11
2.176
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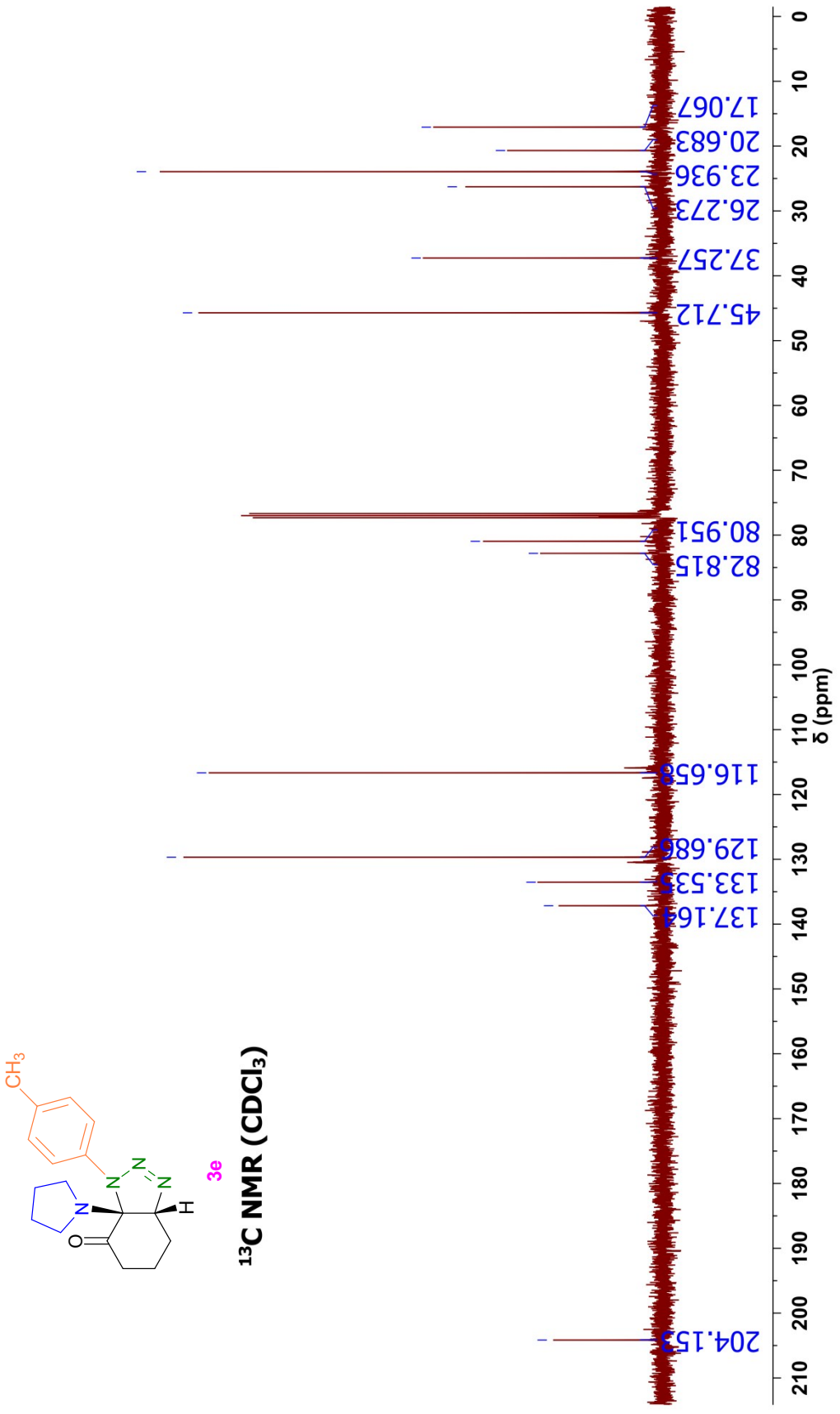
1.528
1.414
6.43
1.09
δ (ppm)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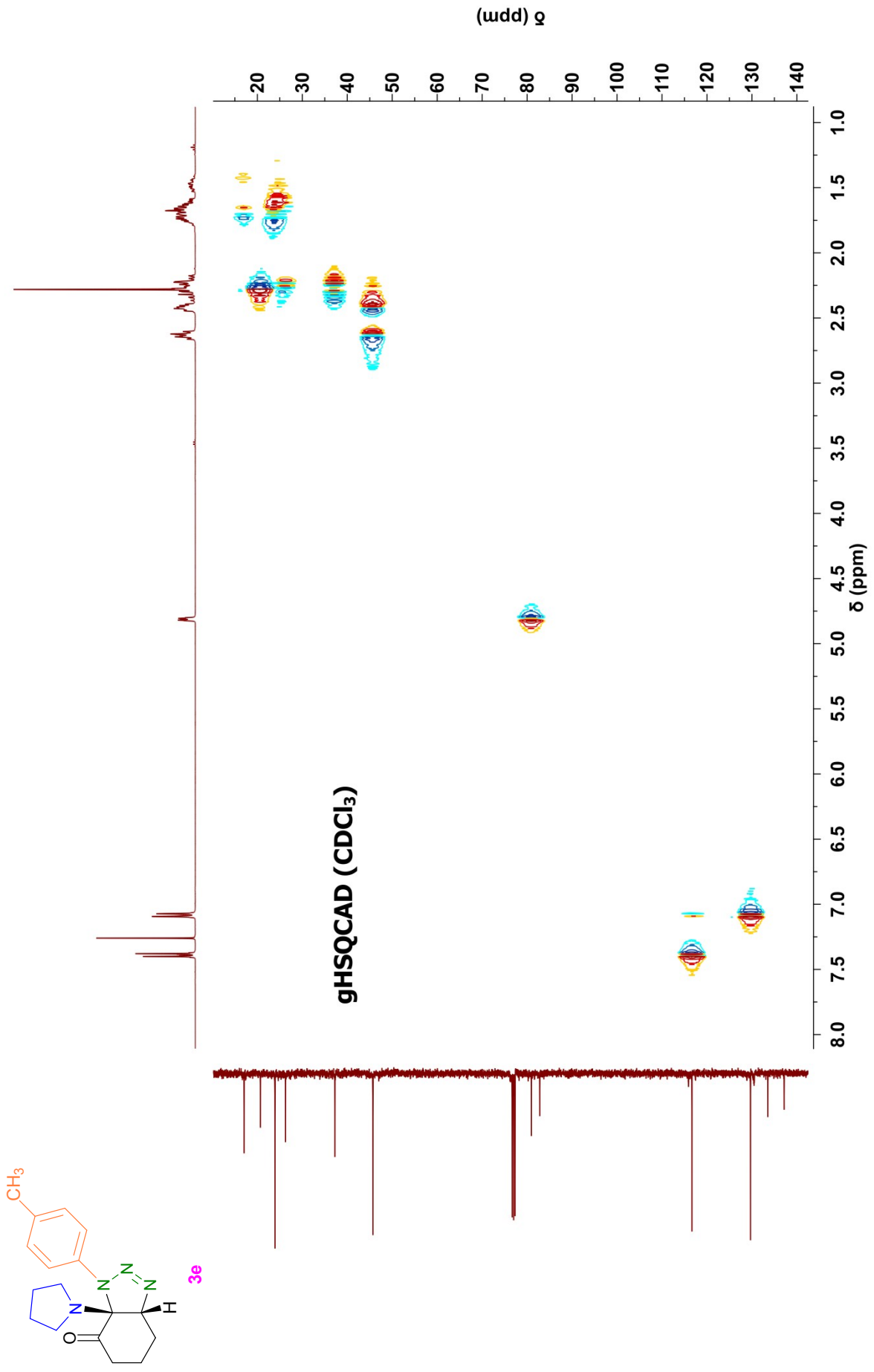
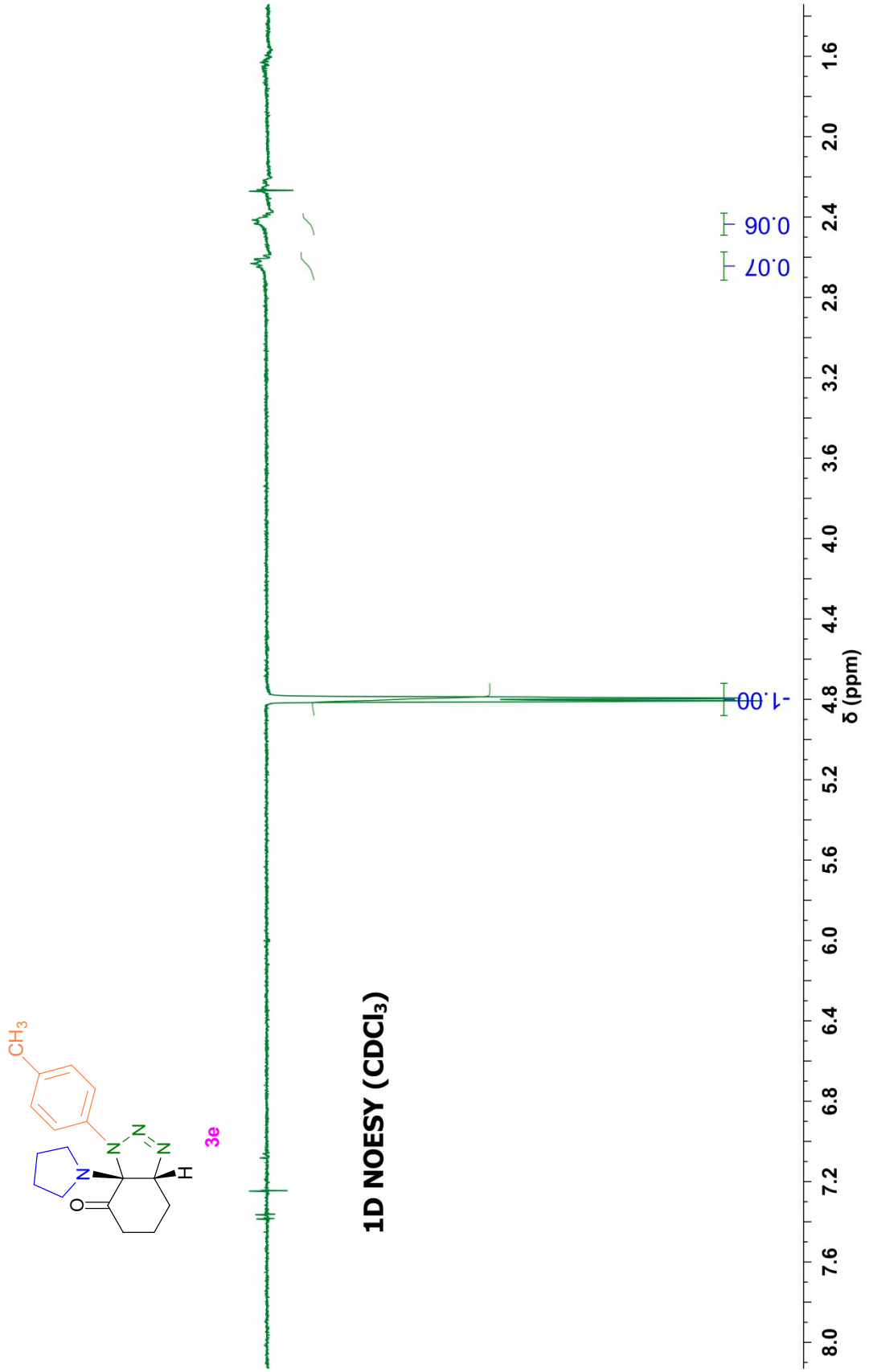
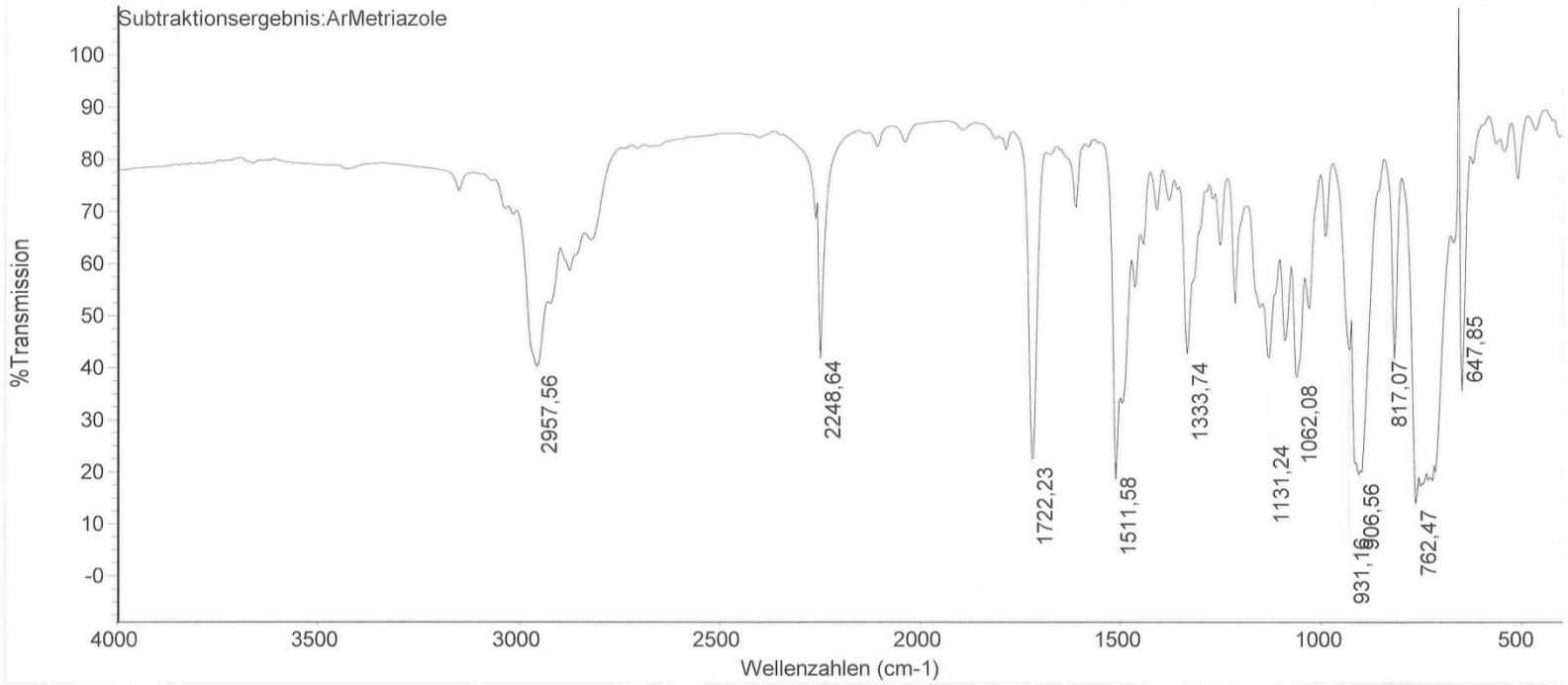
23.936
26.273
37.257
45.712
80.951
82.815
116.658
129.686
133.533
137.164
204.153
δ (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
^{13}C NMR (CDCl$_3$)
3e
CH$_3$
N
N
N
H
O


gHSQCAD (CDCl3)
δ (ppm)
δ (ppm)
CH3
N
N
N
N
H
O
3e


1D NOESY ($CDCl_3$)
3e
1.00
0.07
0.06
δ (ppm)
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6



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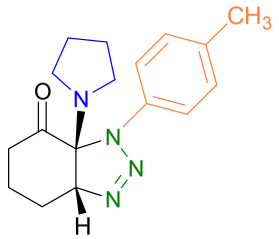
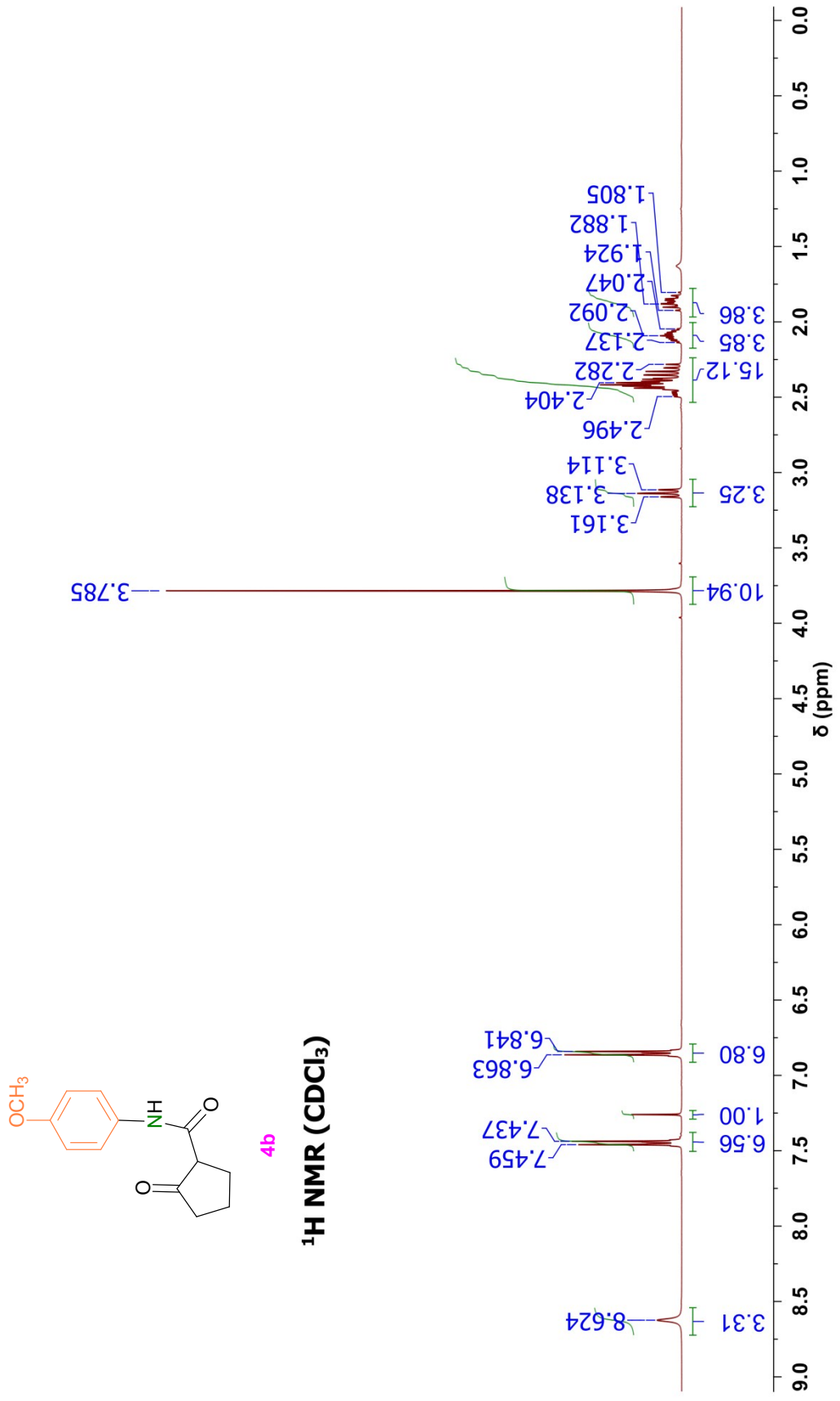


3e


OCH3
NH
O
O
4b
1H NMR (CDCl3)
δ (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
8.624
7.459
7.437
6.841
6.863
3.785
3.161
3.138
3.114
2.496
2.404
2.282
2.137
2.092
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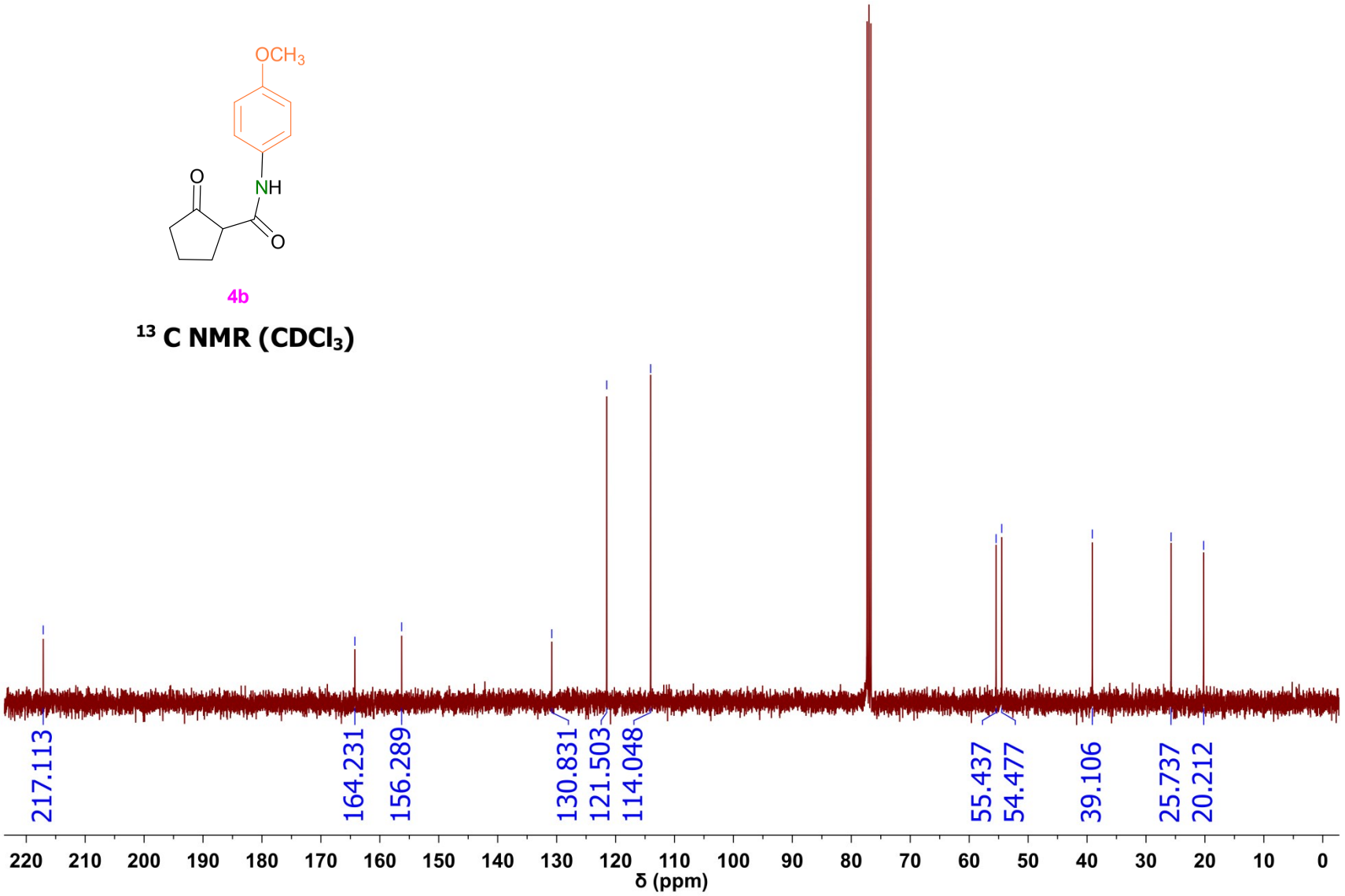
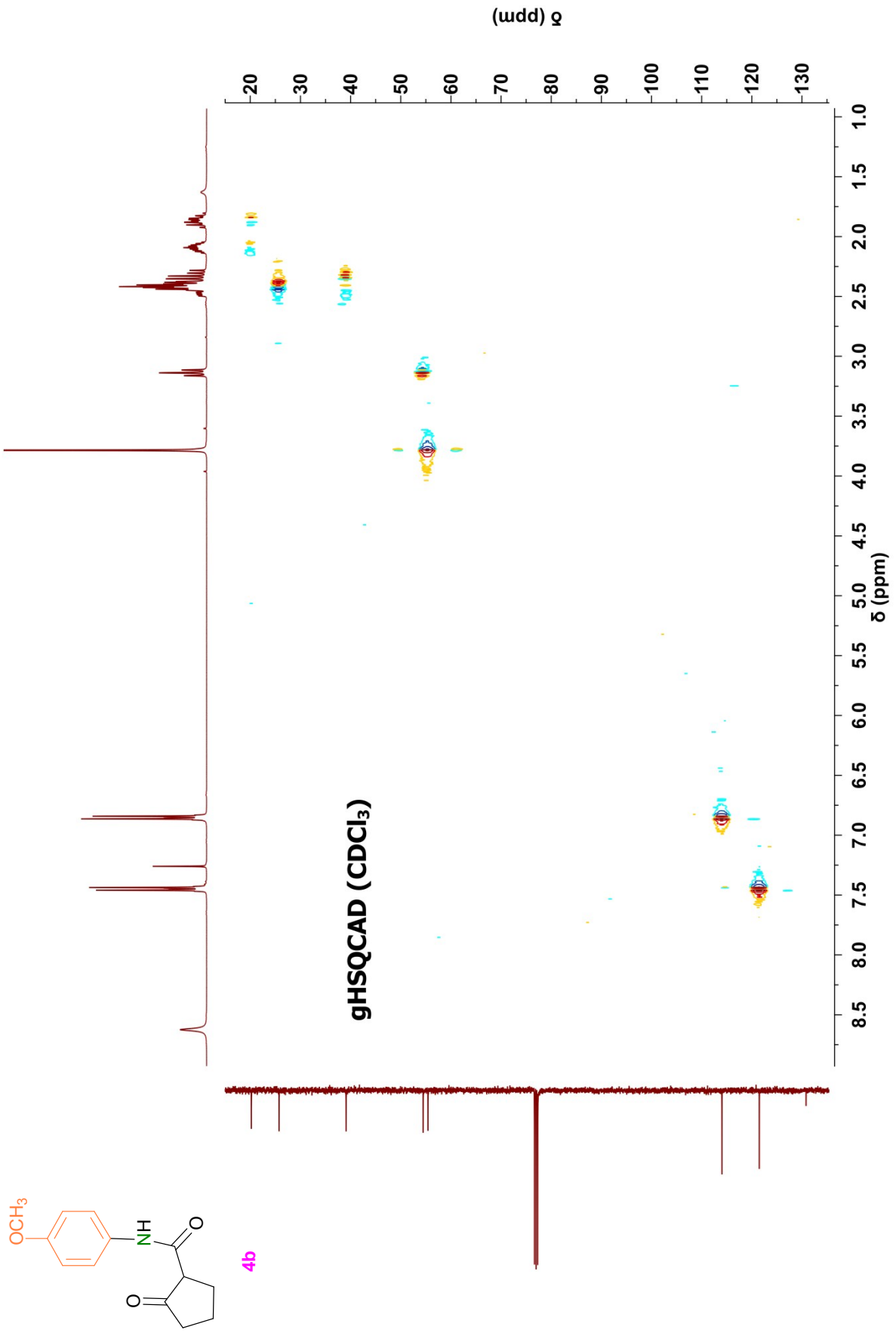
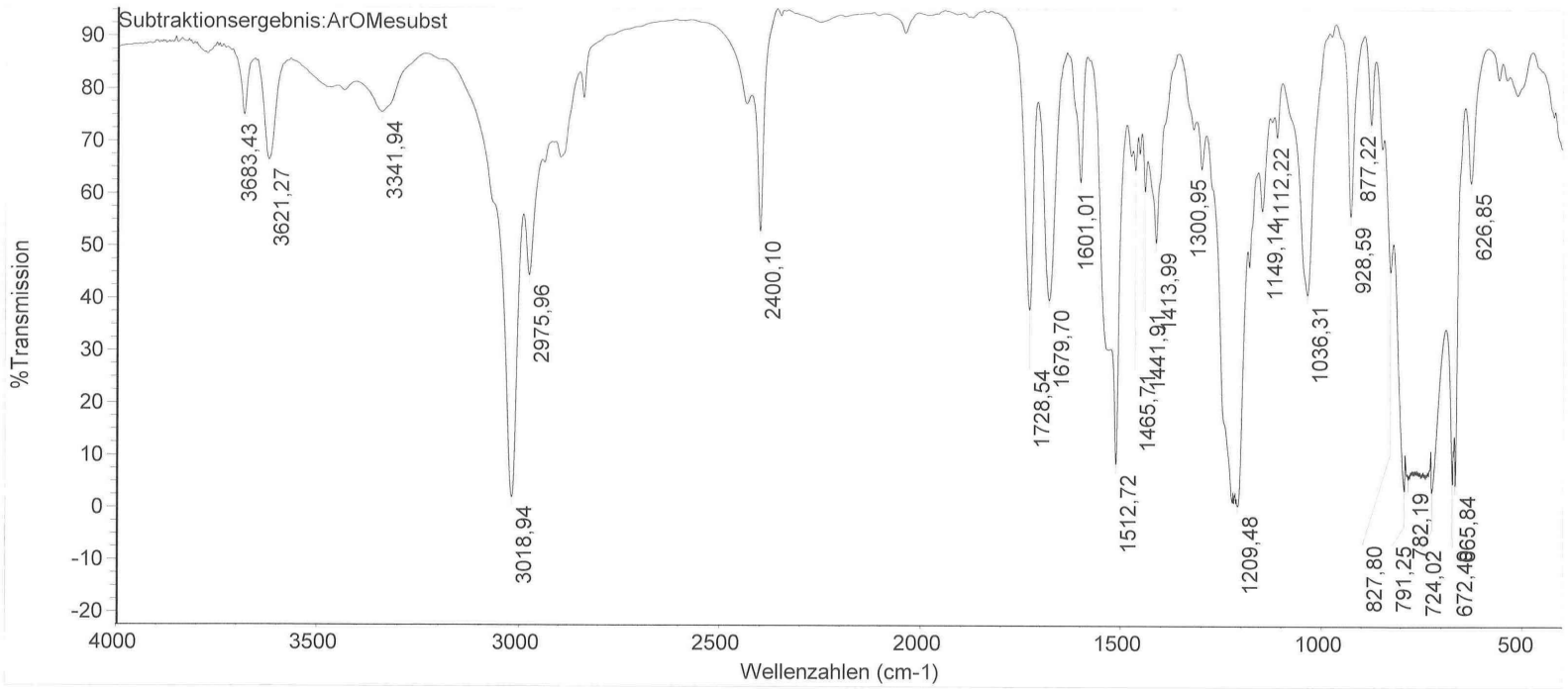
15.12
3.85
3.86


OCH3
O
NH
O
4b
13 C NMR (CDCl3)
217.113
164.231
156.289
130.831
121.503
114.048
55.437
54.477
39.106
25.737
20.212
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ (ppm)


gHSQCAD (CDCl3)
δ (ppm)
δ (ppm)
OCH3
NH
O
O
4b



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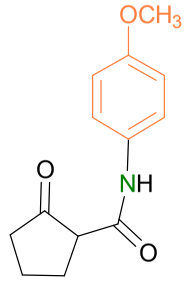
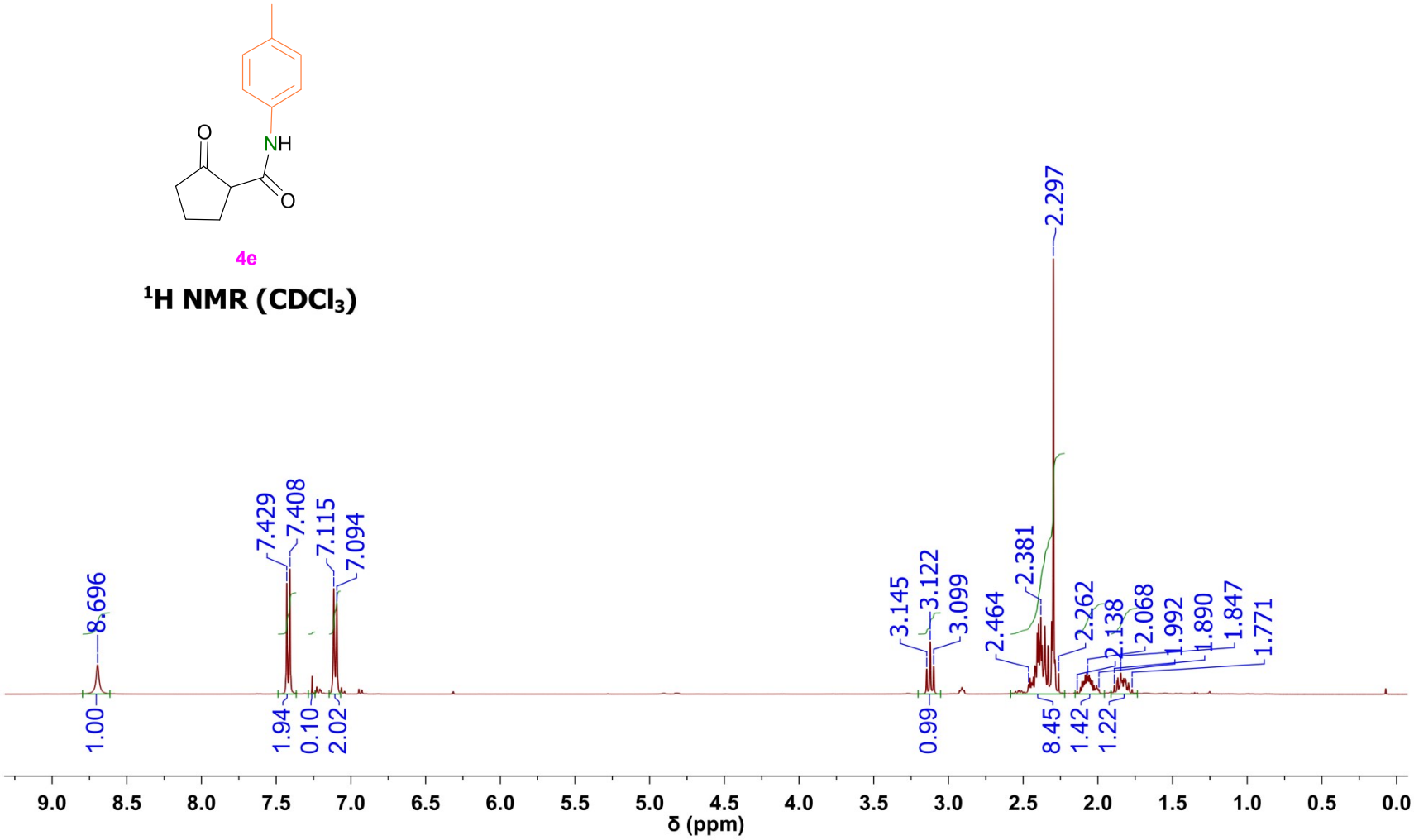
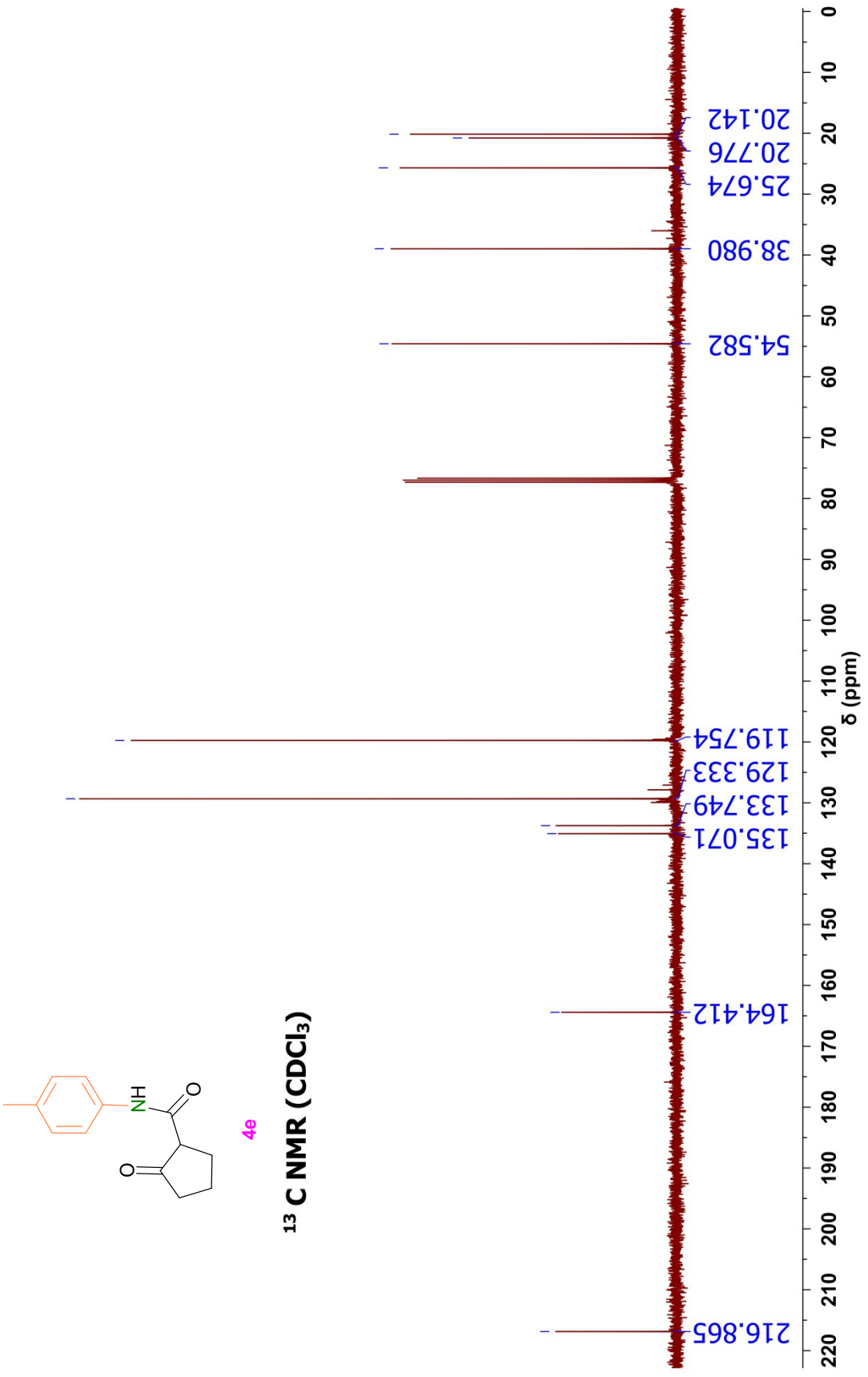
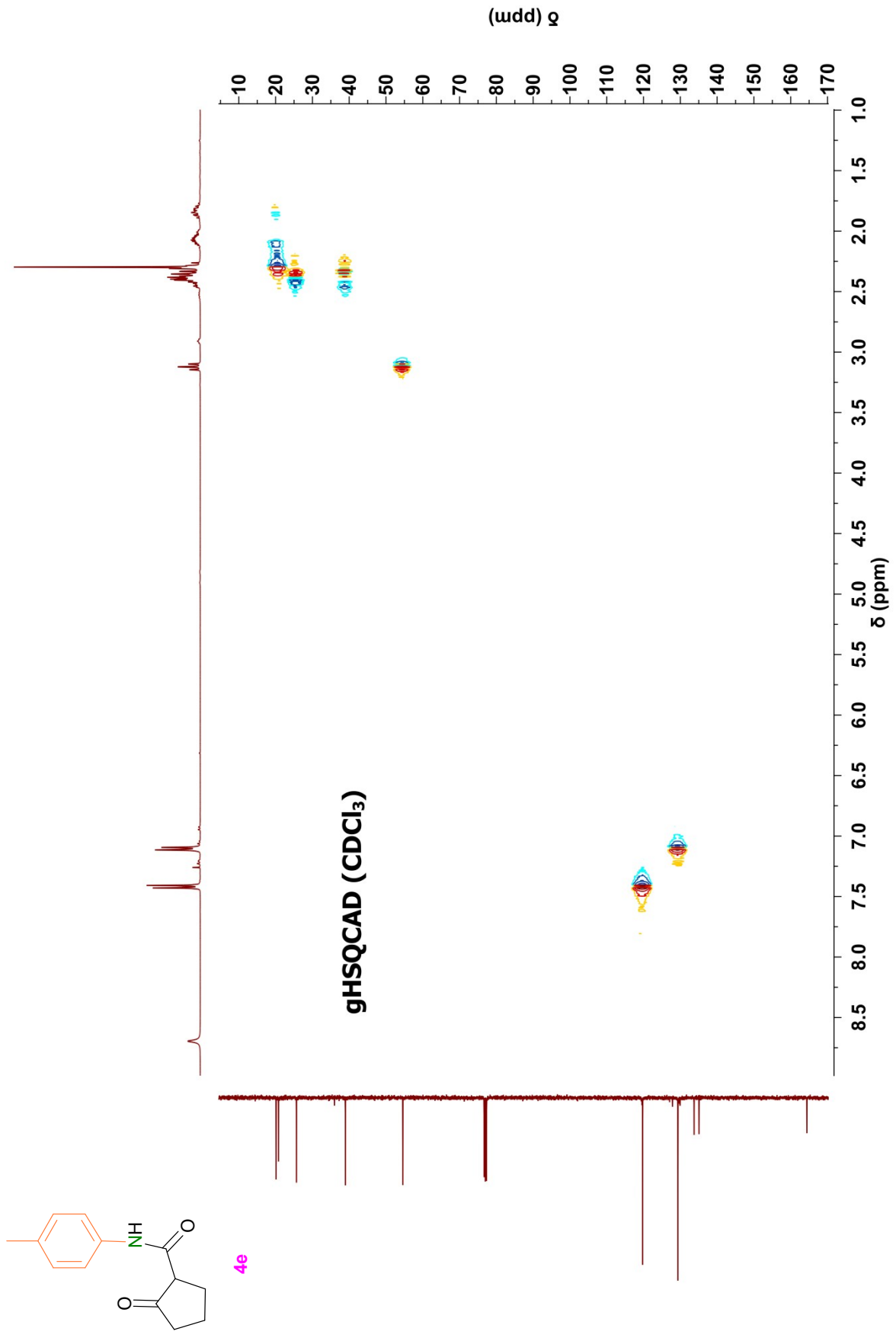
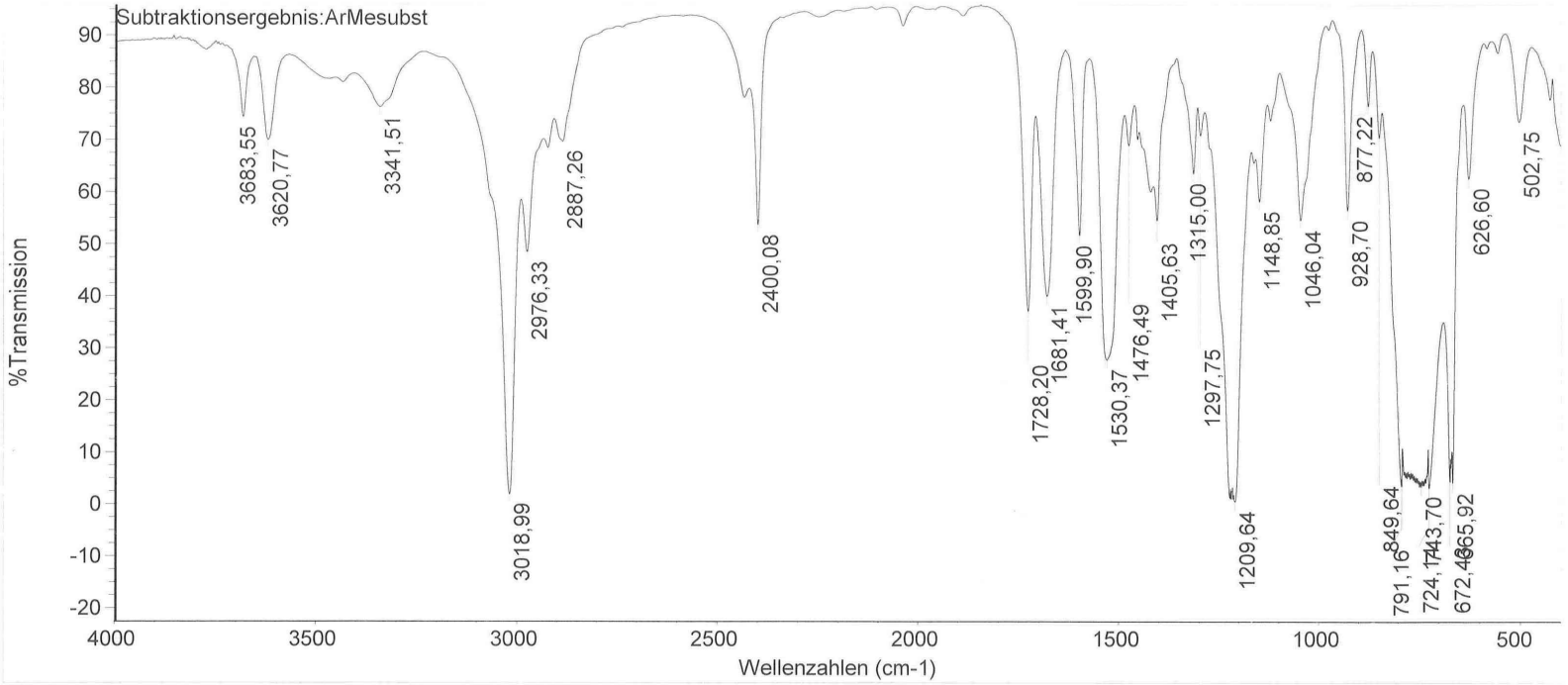


4b


4e
^{1}H NMR (CDCl$_3$)
8.696
7.429
7.408
7.115
7.094
3.145
3.122
3.099
2.464
2.381
2.297
2.262
2.138
2.068
1.992
1.890
1.847
1.771
1.00
1.94
0.10
2.02
0.99
8.45
1.42
1.22
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)


^{13}C NMR ($CDCl_3$)
4e
216.865
164.412
135.071
133.749
129.333
119.754
54.582
38.980
25.674
20.776
20.142
δ (ppm)


gHSQCAD (CDCl3)
δ (ppm)
δ (ppm)
4e



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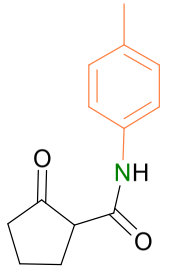
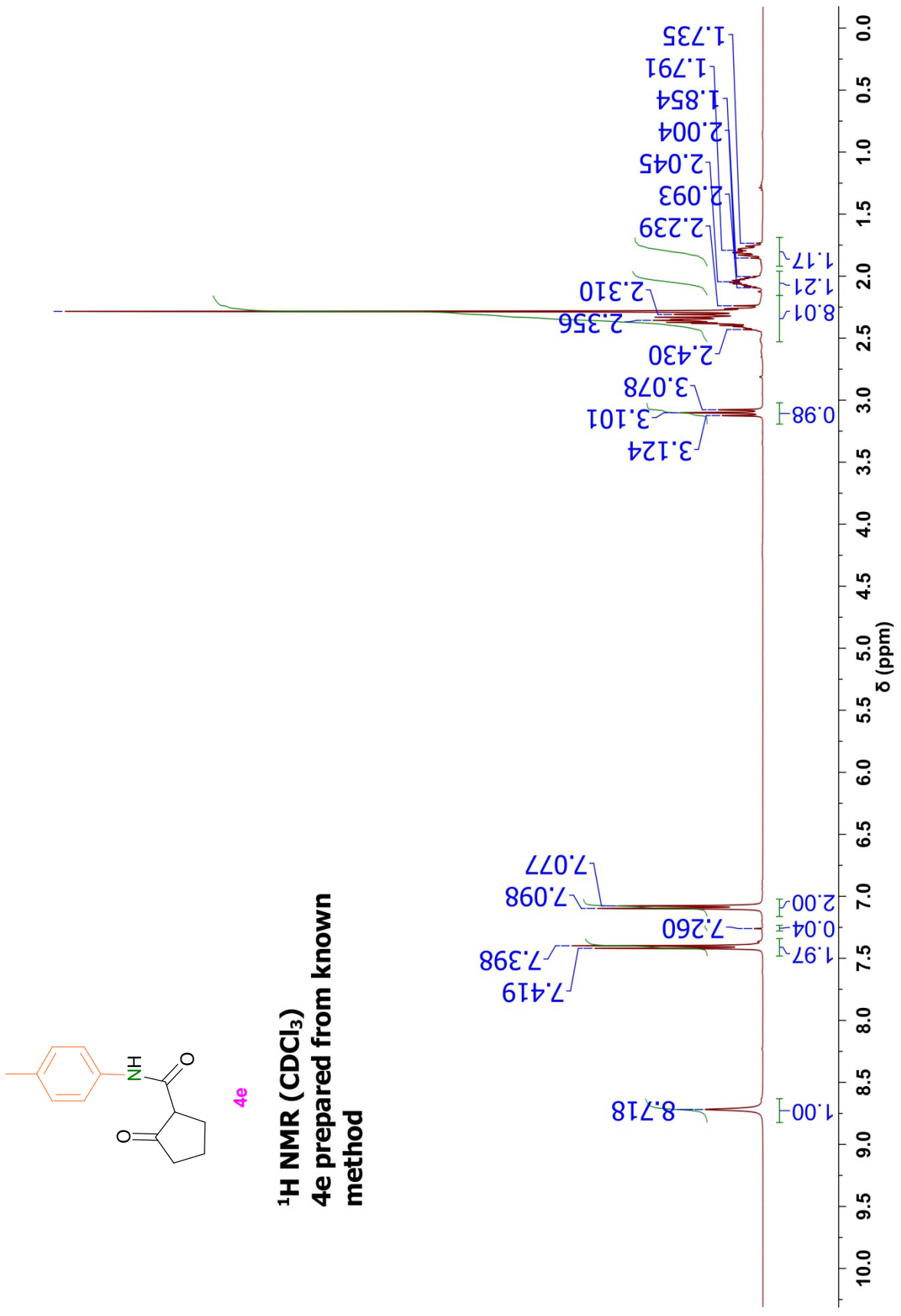
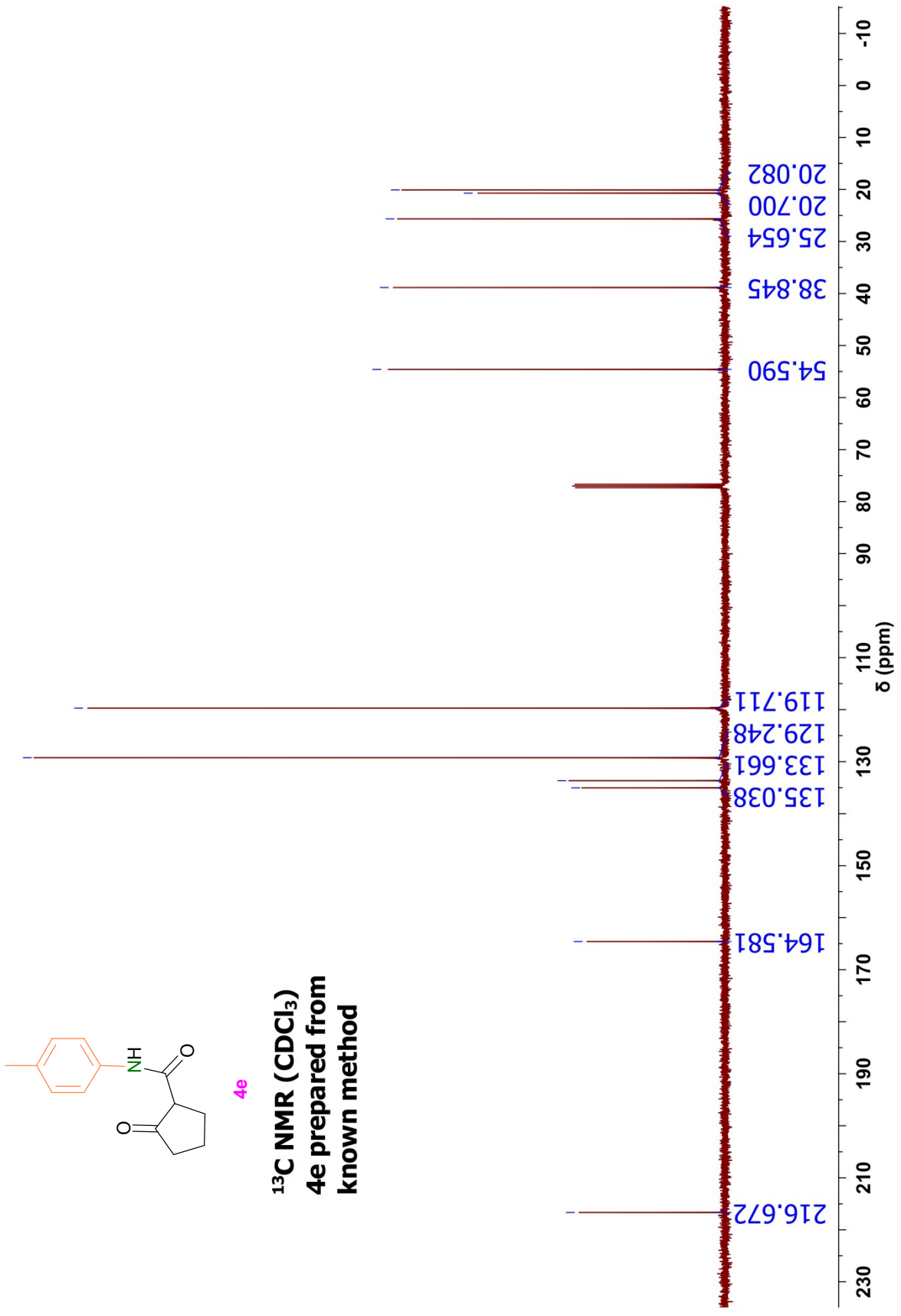
Position:	665,92	Intensität:	3,359
Position:	672,43	Intensität:	3,624
Position:	724,14	Intensität:	3,036
Position:	743,70	Intensität:	3,187
Position:	791,16	Intensität:	3,424



4e


1H NMR (CDCl3)
4e prepared from known method
4e
8.718
7.419
7.398
7.260
7.098
7.077
3.124
3.101
3.078
2.430
2.356
2.310
2.239
2.093
2.045
2.004
1.854
1.791
1.735
1.00
1.97
0.04
2.00
0.98
8.01
1.21
1.17
δ (ppm)


20.082
20.700
25.654
38.845
54.590
119.711
129.248
133.661
135.038
164.581
216.672
δ (ppm)
4e
^{13}C NMR (CDCl$_3$)
4e prepared from
known method