Electronic Supplementary Material (ESI) for Dalton Transactions.

A ferrocene-based pseudopeptide chiroptical switch

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Supplementary information

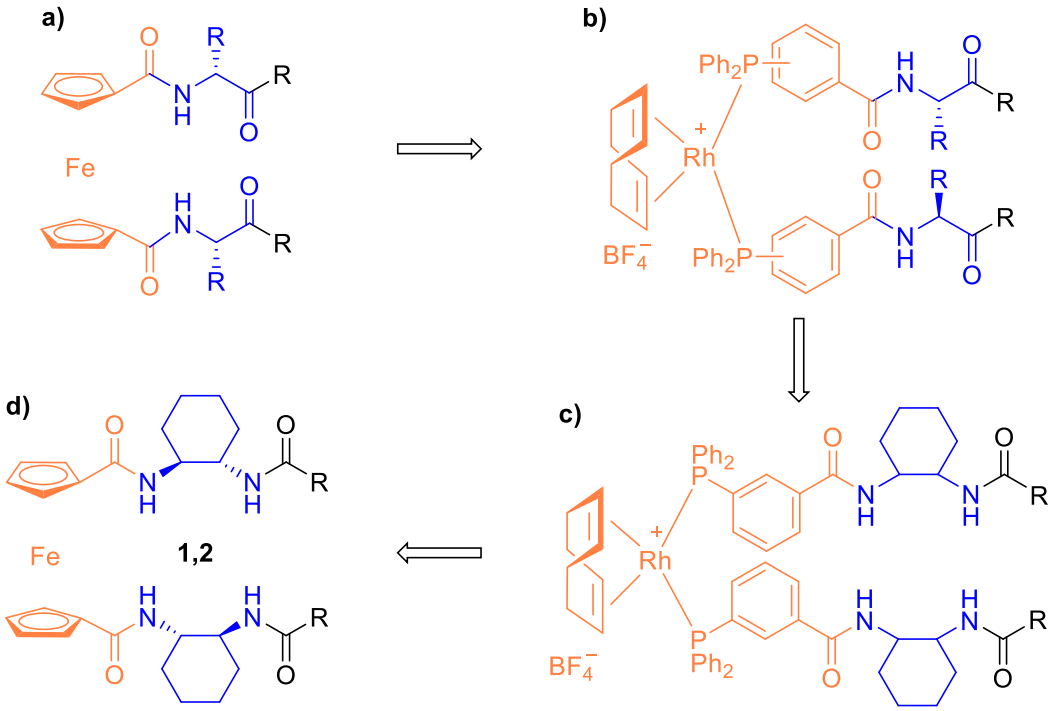
1 Contents

2 Supplement layout description

The supplement is divided in numerated chapters which correspond to one or more figures, tables, or other types of data. In the manuscript the relevant chapters are referenced by their respective numbers. Ctrl+click on a title or subtitle in the contents table enables fast access to the relevant chapter.

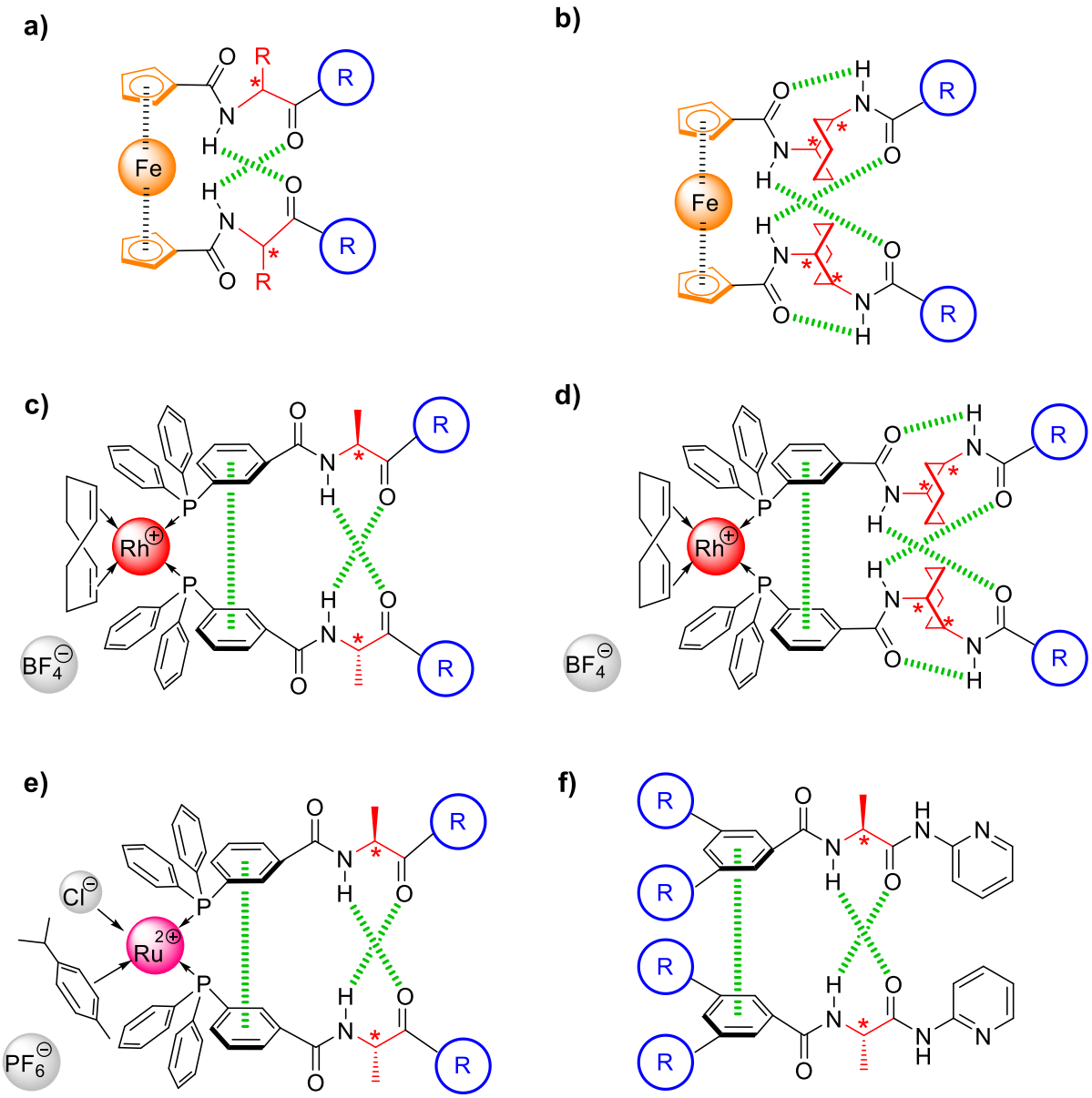
3 Development of ferrocene amides

3.1 History of this work



a) Ferrocene amino acids[1]; b) amino acid phosphine catalysts;[2] c) cyclohexane amide catalysts;[3] d) ferrocene amides (**1, 2**), this work.

3.2 Systems with similar stereochemistry



Examples of our work containing systems in which *L* amino acids/amides induce *P* helical chirality on ferrocene or on stacked *m*-disubstituted phenyls:

a) Ferrocene amino acid compounds[1]

b) Ferrocene amide compounds (this work)

c) Triphenylphosphine Rh amino acid catalysts[4]

d) Triphenylphosphine Rh amide catalysts[3]

e) Triphenylphosphine amino acid Ru complexes[5]

f) Triphenylphosphine amino acid pyridine zinc complexes[6]

4 Experimental

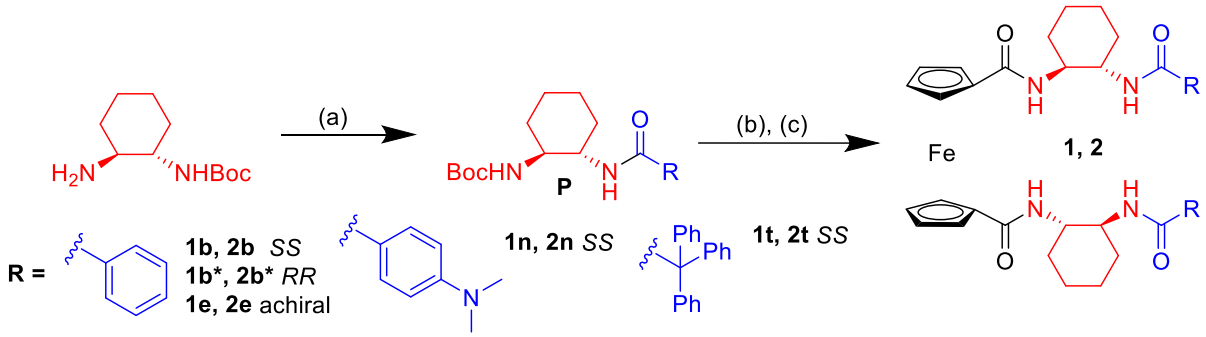
4.1 Reagent abbreviations

TBTU: 2-(1H-Benzotriazole-1-yl)-1,1,3,3-tetramethylaminium tetrafluoroborate

HOBT: 1-Hydroxybenzotriazole hydrate

DIPEA: N,N-Diisopropylethylamine

4.2 Synthesis



(a) TBTU/HOBt, DCM, 24-48 h, r.t. (b) TFA/DCM 1/1, 2 h, r.t. (c) TBTU/HOBt, 1/1,1' ferrocenecarboxylic acid, DCM, 24-48 h, r.t.

4.3 Precursors

Synthesis of all precursors except $\mathbf{P_a}$ and $\mathbf{P_b}$* is described in the literature.[3]

Ph-cyh-boc ($\mathbf{P_b}$). Benzoic acid (125 mg 1.00 mmol), TBTU (325 mg, 1.00 mmol), HOBt (135 mg, 1.000 mmol), DIPEA (0.300 mL, 2.04 mmol), (1*S*,2*S*)-*trans*-*N*-Boc-1,2-cyclohexanediamine (215 mg, 1.00 mmol) and CH_2Cl_2 (50 ml). Yield: 282 mg (89%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm: 7.89 – 7.76 (m, 2H), 7.50 – 7.33 (m, 3H), 7.07 (d, J = 6.7 Hz, 1H), 4.68 (d, J = 8.6 Hz, 1H), 3.85 – 3.68 (m, 1H), 3.63 – 3.42 (m, 1H), 2.27 (d, J = 13.3 Hz, 1H), 2.02 (d, J = 10.0 Hz, 1H), 1.87 – 1.70 (m, 2H), 1.44 – 1.17 (m, 4H) 1.32 (s, 9H).

Ph-cyh*-boc ($\mathbf{P_b}$*) Benzoic acid (125 mg 1.00 mmol), TBTU (325 mg, 1.00 mmol), HOBt (135 mg, 1.000 mmol), DIPEA (0.300 mL, 2.04 mmol), (1*R*,2*R*)-*trans*-*N*-Boc-1,2-cyclohexanediamine (215 mg, 1.00 mmol) and CH_2Cl_2 (50 ml). Yield: 309 mg (97%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.87 – 7.83 (m, 2H), 7.48 (t, *J*=7.3, 1H), 7.41 (t, *J*=7.6, 2H), 7.10 (d, *J*=7.4, 1H), 4.69 (d, *J*=8.7, 1H), 3.82 – 3.72 (m, 1H), 3.59 – 3.51 (m, 1H), 2.29 (d, *J*=13.4, 1H), 2.04 (d, *J*=13.2, 1H), 1.86 – 1.74 (m, 2H), 1.43 – 1.22 (m, 13H).

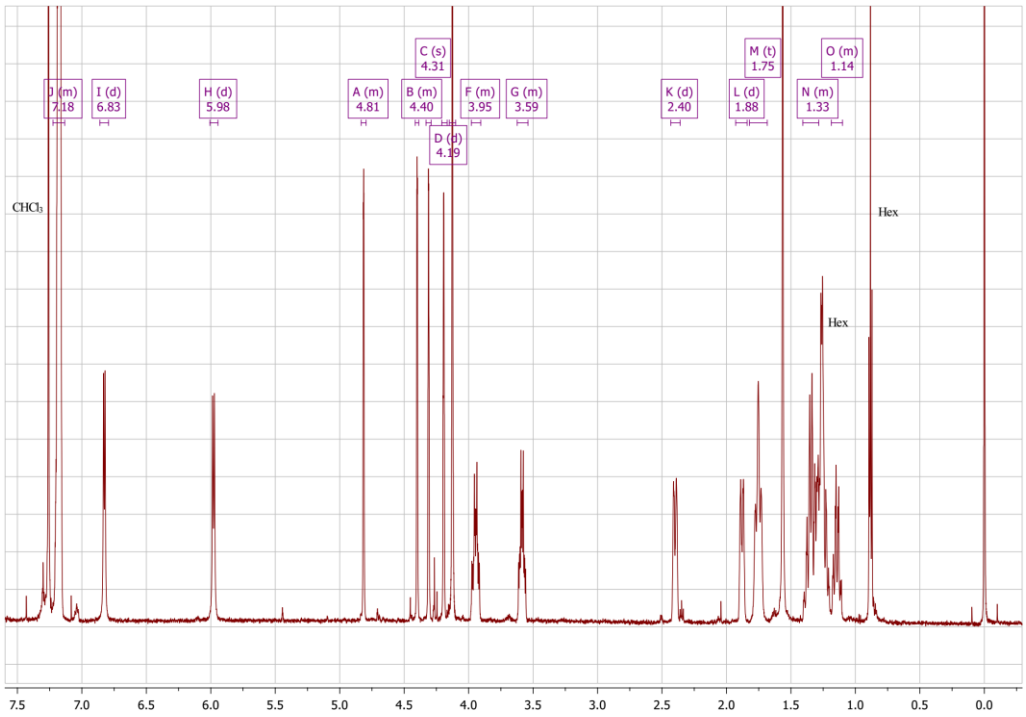
$\mathbf{Ph_N}$-cyh-Boc ($\mathbf{P_n}$). 4-Dimethylaminobenzoic acid (132 mg, 0,80 mmol), TBTU (258 mg, 0,80 mmol), HOBt (101 mg, 0,80 mmol), DIPEA (0,240 mL, 1,63 mmol), (1*S*,2*S*)-*trans*-*N*-Boc-1,2-cikloheksadiamin (171 mg, 0,80 mmol), CH_2Cl_2 (50 ml). Iskorištenje: 230 mg (80%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm: 1H NMR (300 MHz, CDCl3) δ 7,71 (d, J = 8,9 Hz, 2H), 6,77 (d, J = 7,5 Hz, 1H), 6,64 (d, J = 9,0 Hz, 2H), 4,72 (d, J = 8,8 Hz, 1H), 3,83 – 3,66 (m, 1H), 3,58 – 3,38 (m, 1H), 3,00 (s, 6H), 2,23 (d, J = 12,9 Hz, 1H), 2,03 (d, J = 11,1 Hz, 1H), 1,84 – 1,71 (m, 2H), 1,32 – 1,09 (m, 4H), 1,33 (s, 9H).

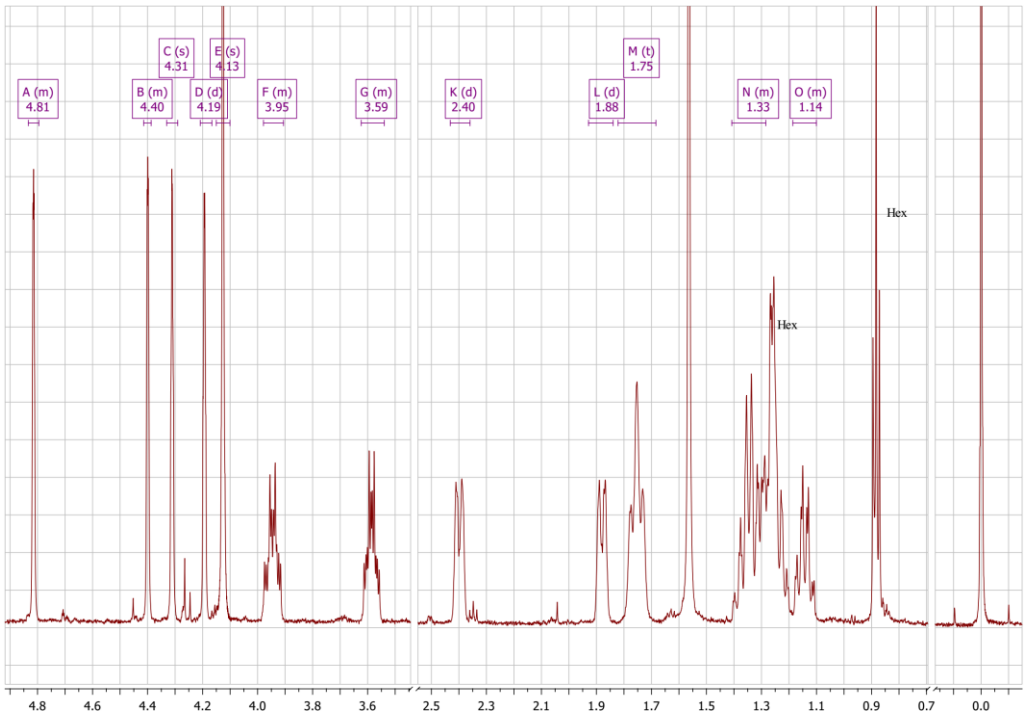
Tph-cyh-boc (P_t). Triphenylacetic acid (242 mg, 0.84 mmol), TBTU (271mg, 0.84 mmol), HOBt (112 mg, 0.84 mmol), DIPEA (0.250 mL, 1.68 mmol), (1*S*,2*S*)-*trans*-*N*-Boc-1,2-cyclohexanediamine (180 mg, 0.84 mmol) and CH_2Cl_2 (50 ml). Yield: 261 mg (65 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm: 7.38 – 7.22 (m, 15H), 6.07 (d, *J* = 7.9 Hz, 1H), 5.06 (d, *J* = 8.1 Hz, 1H), 3.90 – 3.70 (m, 1H), 3.32 – 3.12 (m, 1H), 2.13 – 2.05 (m, 1H), 1.98 (d, *J* = 13.0 Hz, 1H), 1.71 (d, *J* = 9.1 Hz, 2H), 1.39 (s, 9H), 1.33 – 1.01 (m, 4H).

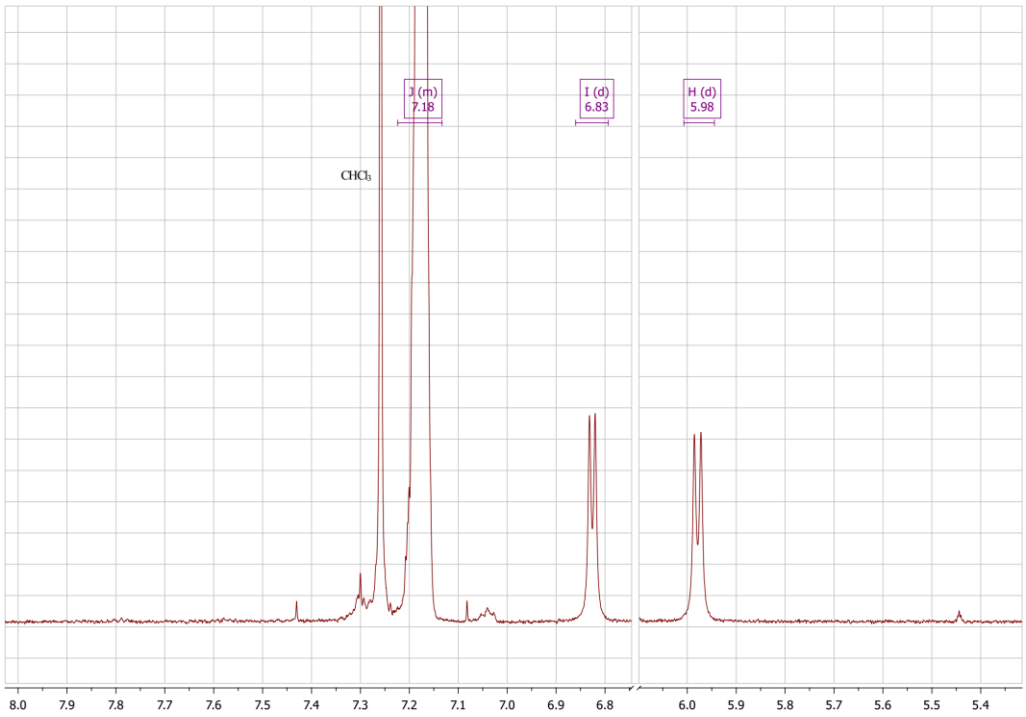
5 Basic NMR spectra (^{1}H, ^{13}C)

5.1 1t

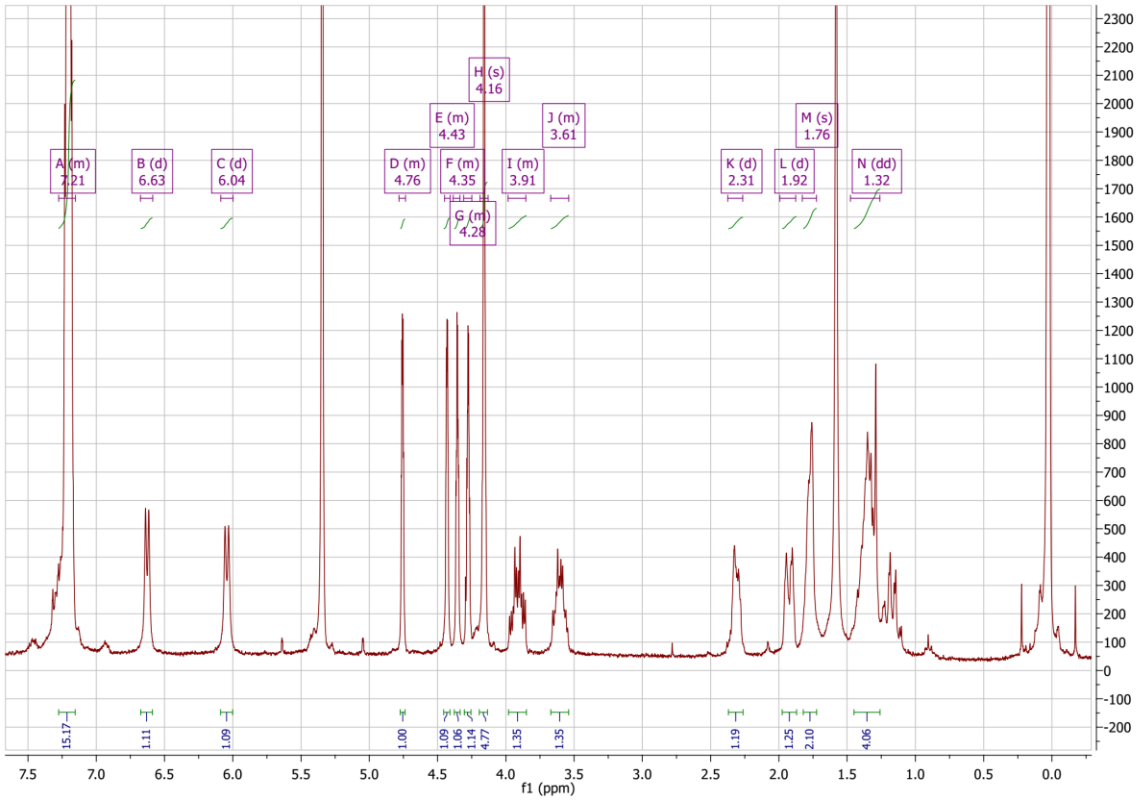
^{1}H NMR (300 MHz, $CDCl_3$)



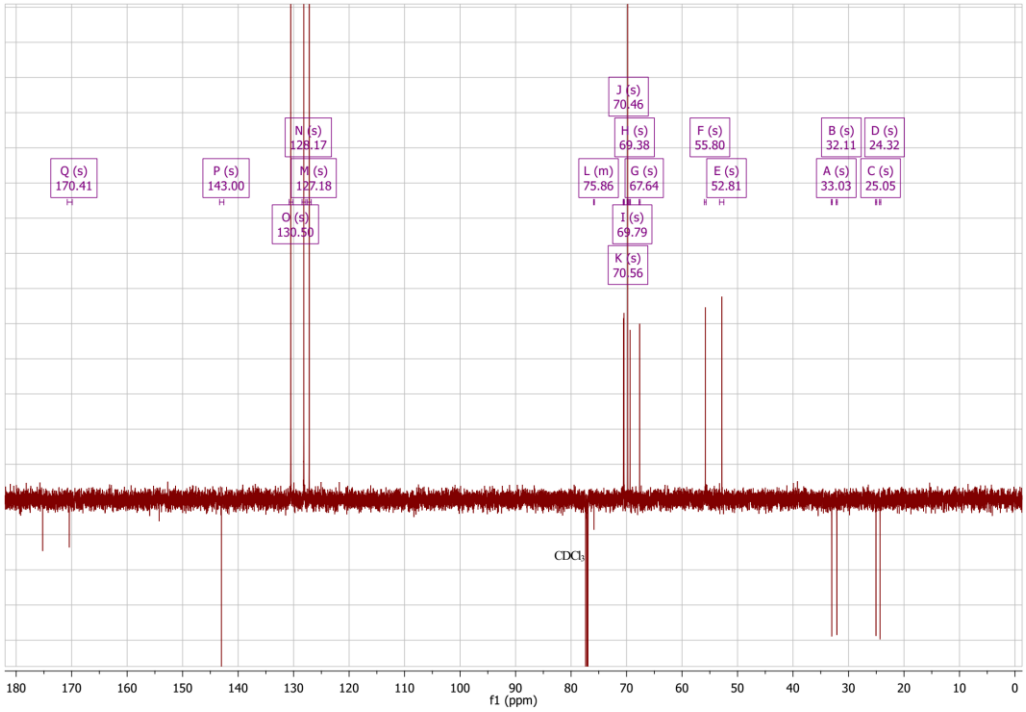


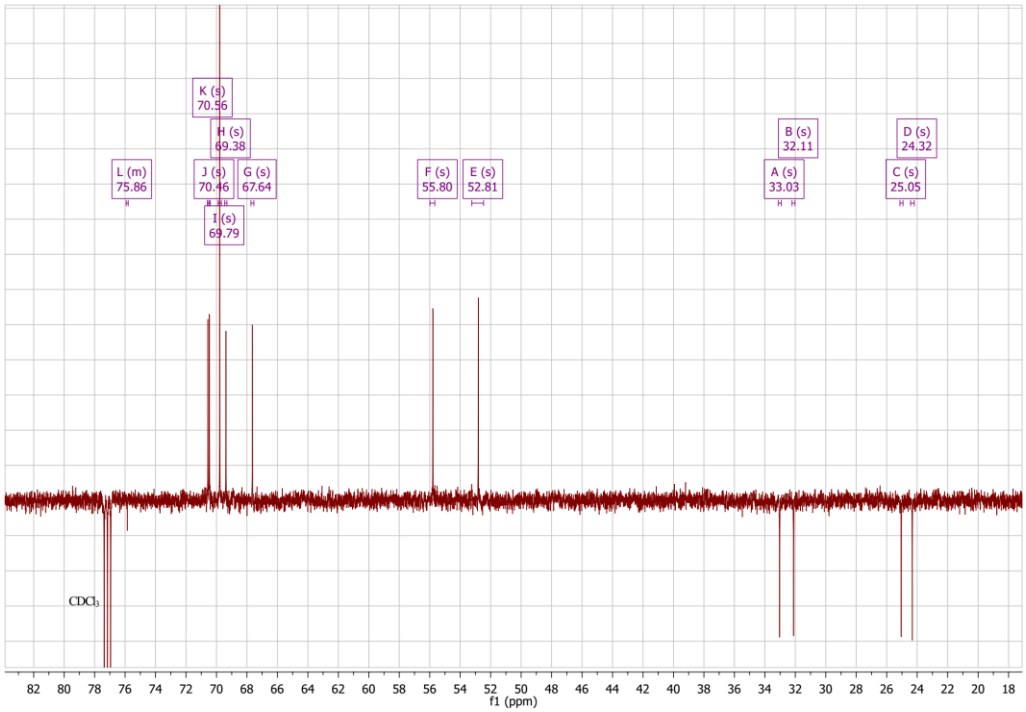


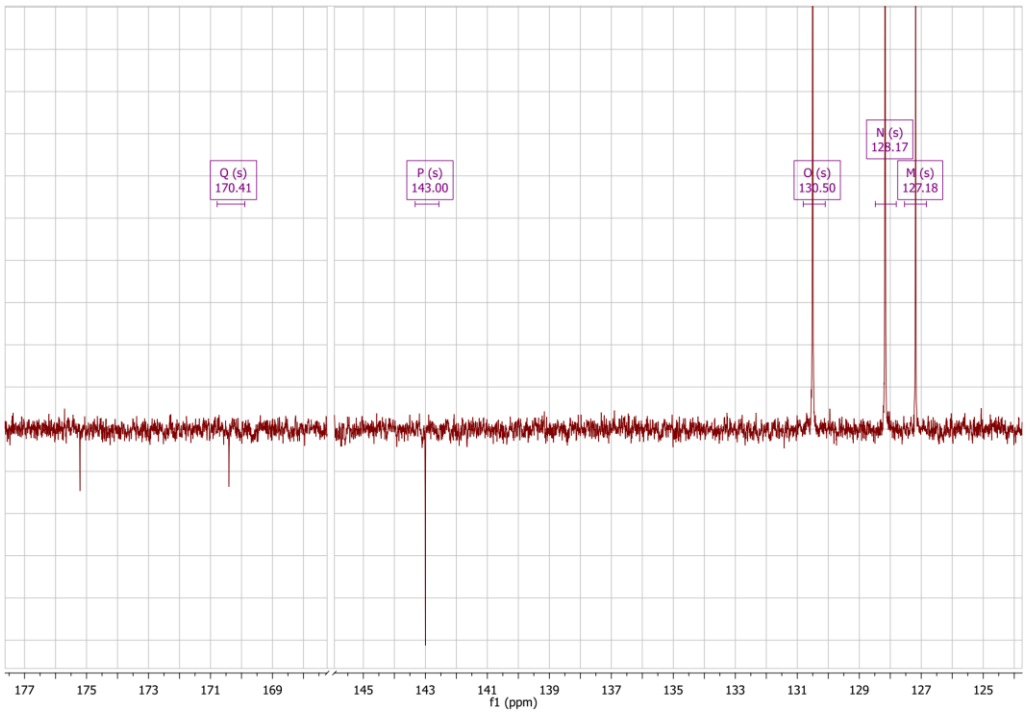
^{1}H NMR (300 MHz, CD_2Cl_2)



^{13}C NMR (151 MHz, $CDCl_3$)

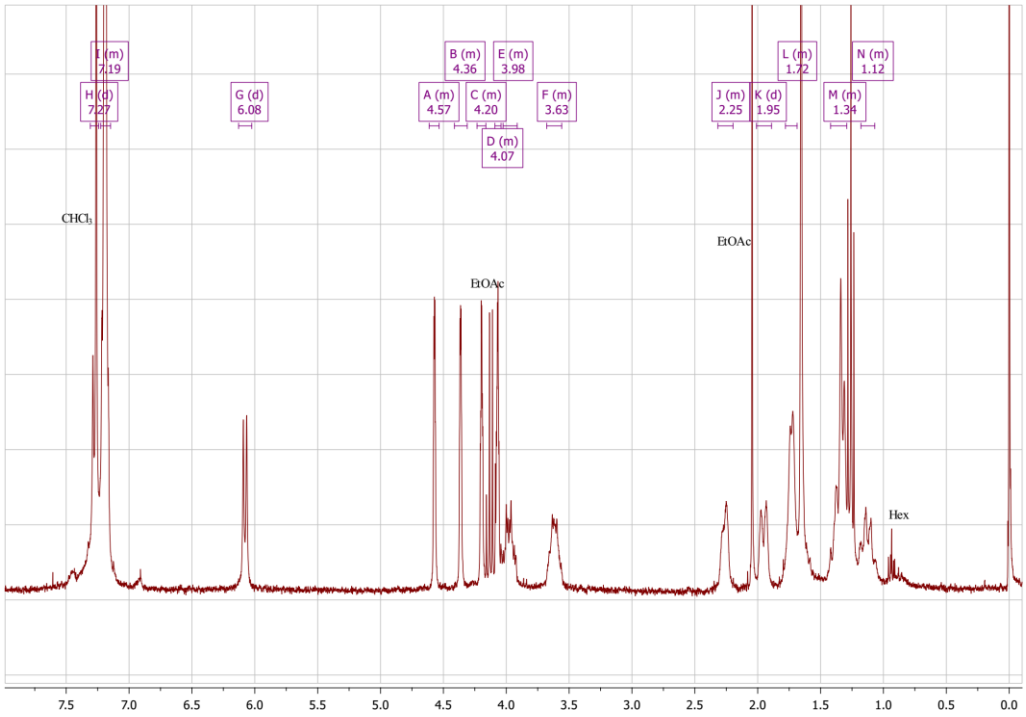


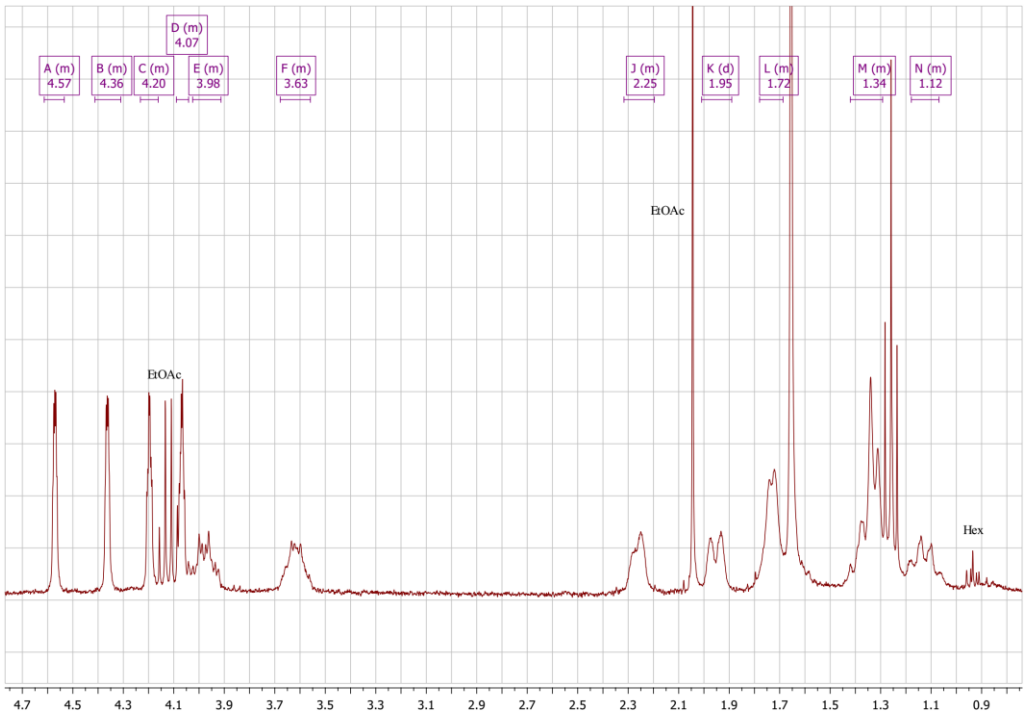


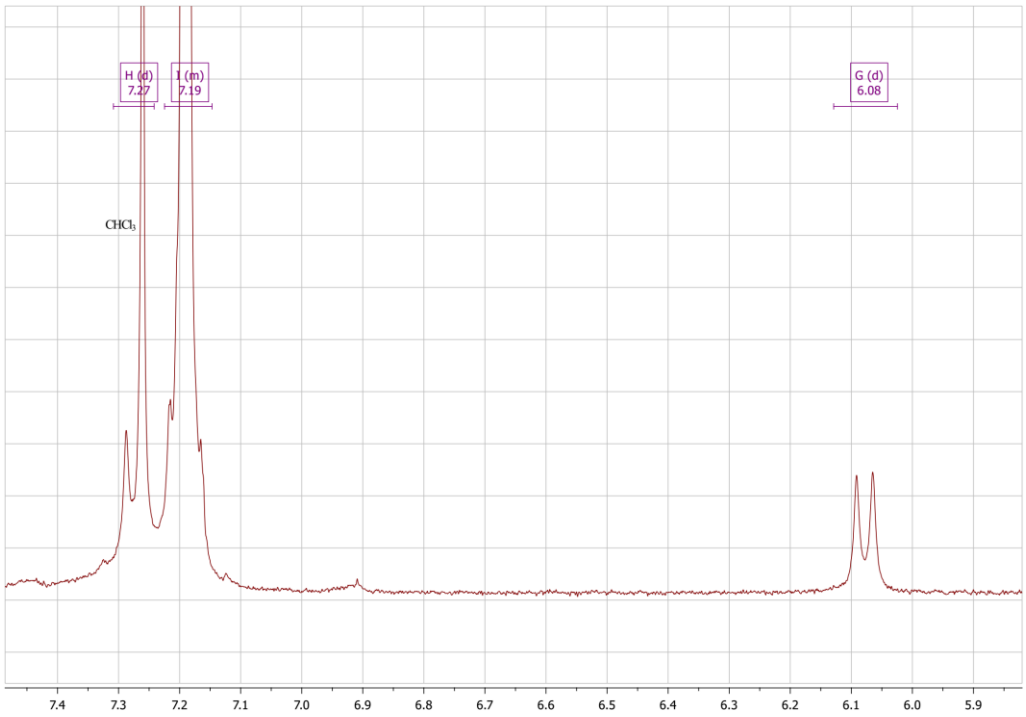


5.2 2t

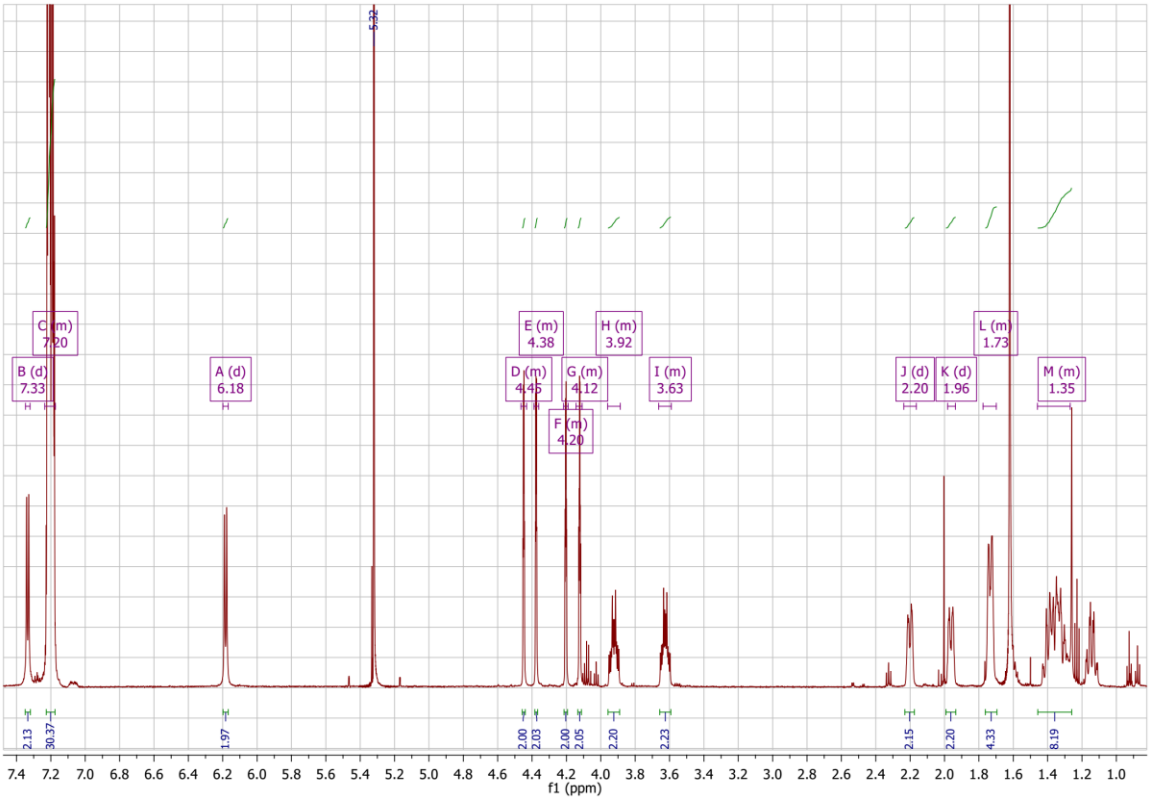
^{1}H NMR (300 MHz, $CDCl_3$)



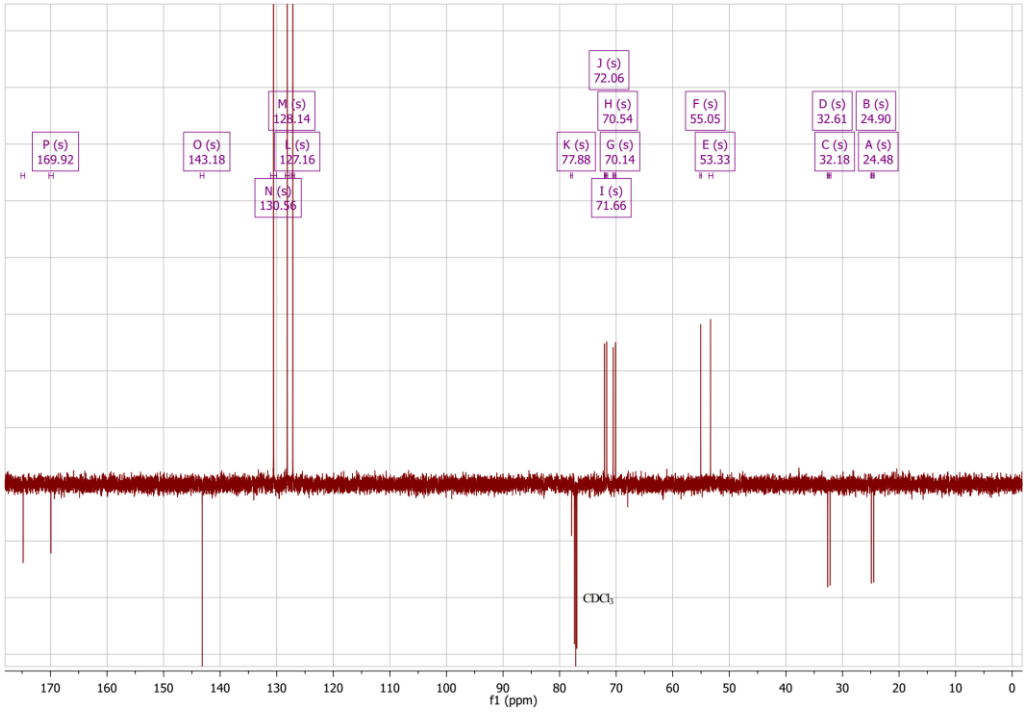

D (m)
4.07
A (m)
4.57
B (m)
4.36
C (m)
4.20
E (m)
3.98
F (m)
3.63
J (m)
2.25
K (d)
1.95
L (m)
1.72
M (m)
1.34
N (m)
1.12
EtOAc
EtOAc
Hex
4.7
4.5
4.3
4.1
3.9
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9

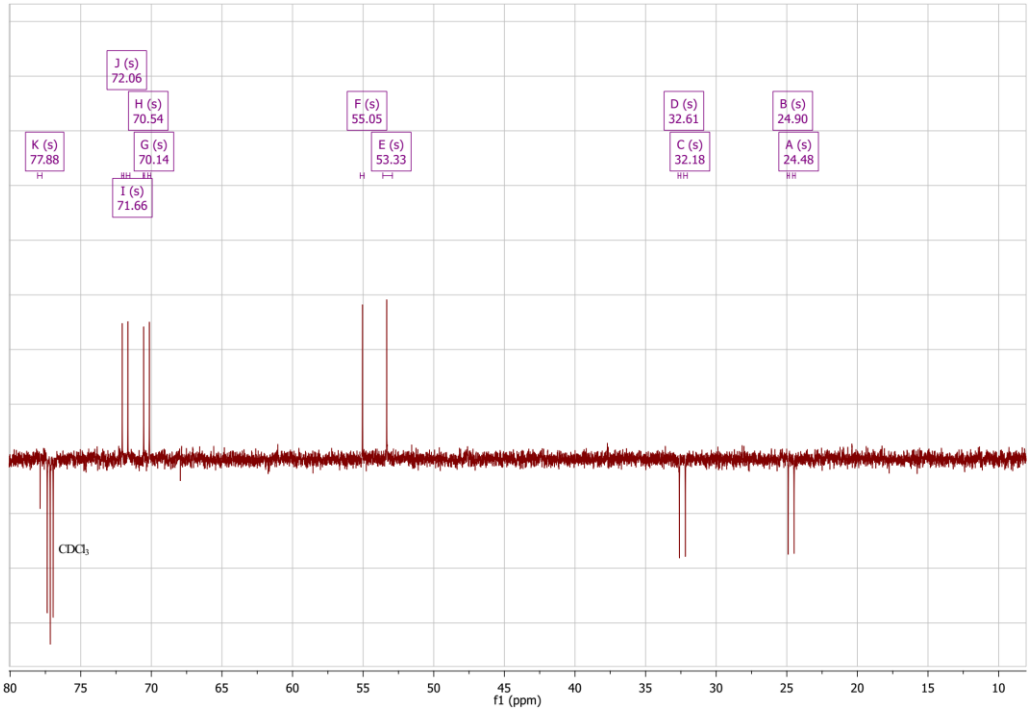

H (d)
7.27
I (m)
7.19
G (d)
6.08
CHCl3
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9

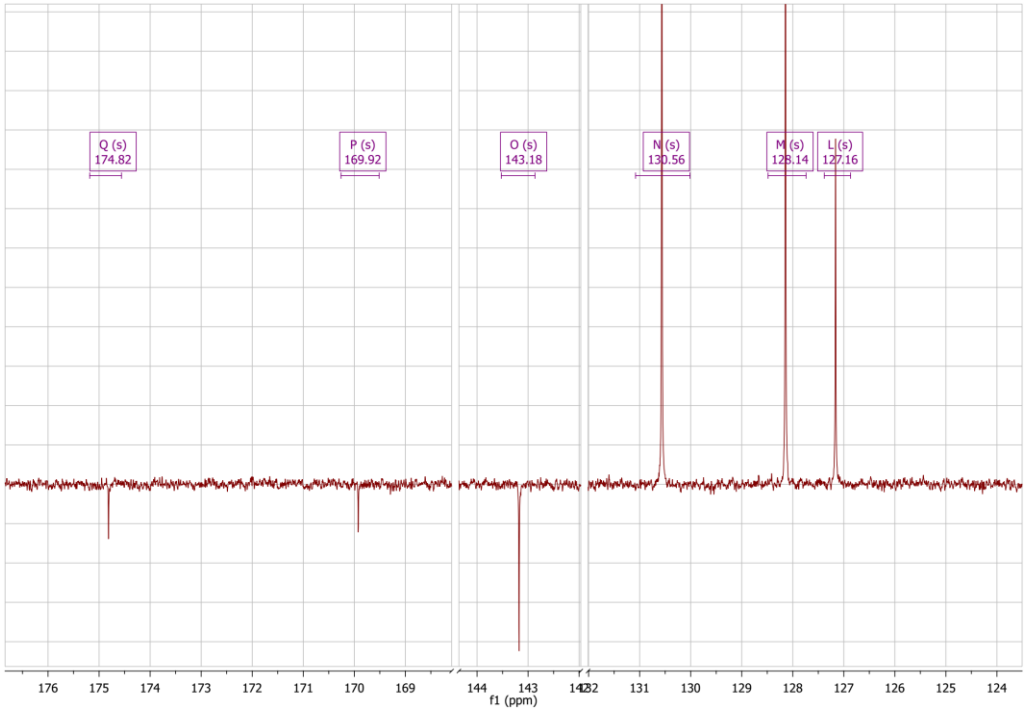
^{1}H NMR (300 MHz, CD_2Cl_2)



^{13}C NMR (151 MHz, $CDCl_3$)

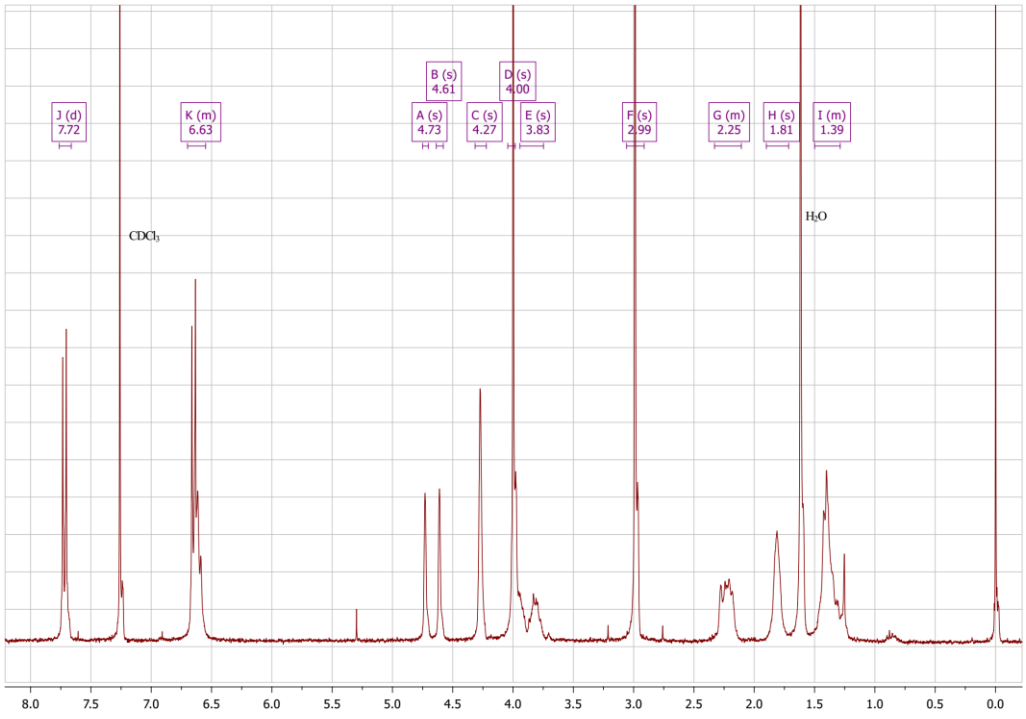


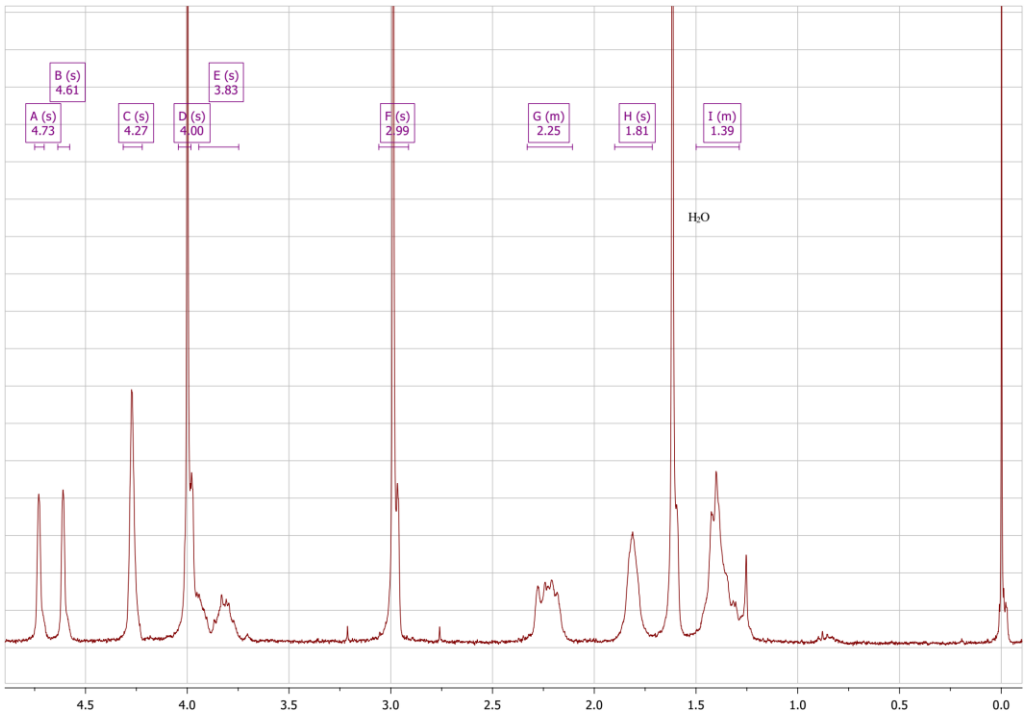

J (s)
72.06
H (s)
70.54
G (s)
70.14
I (s)
71.66
K (s)
77.88
F (s)
55.05
E (s)
53.33
D (s)
32.61
C (s)
32.18
B (s)
24.90
A (s)
24.48
CDCl3
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

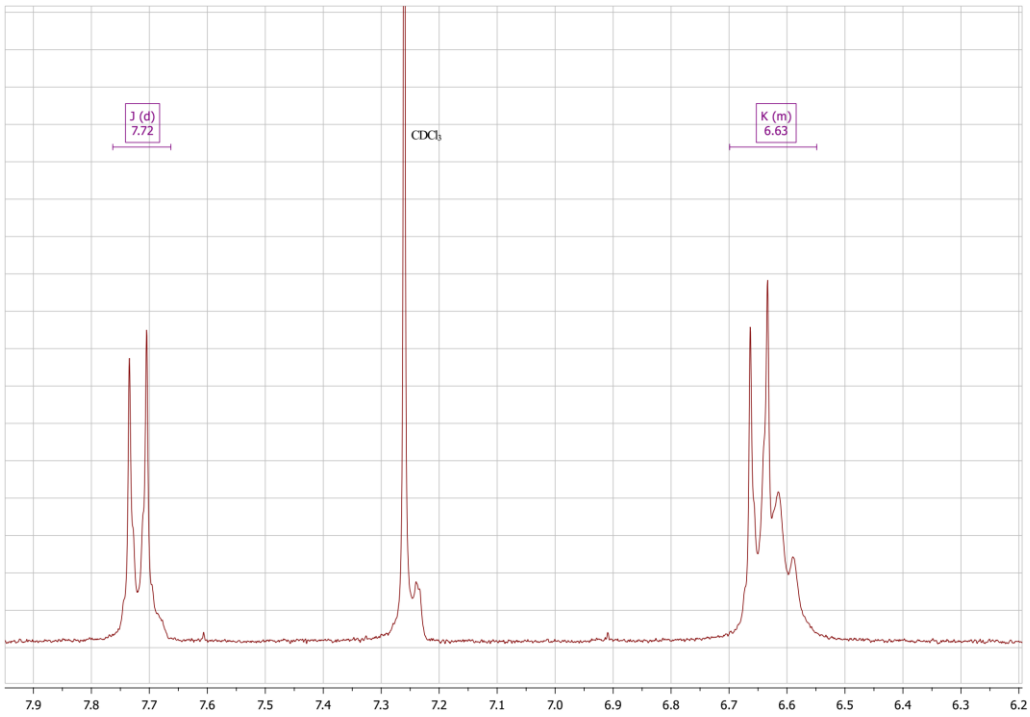

Q (s)
174.82
P (s)
169.92
O (s)
143.18
N (s)
130.56
M (s)
128.14
L (s)
127.16
176 175 174 173 172 171 170 169 144 143 132 131 130 129 128 127 126 125 124
f1 (ppm)

5.3 1n

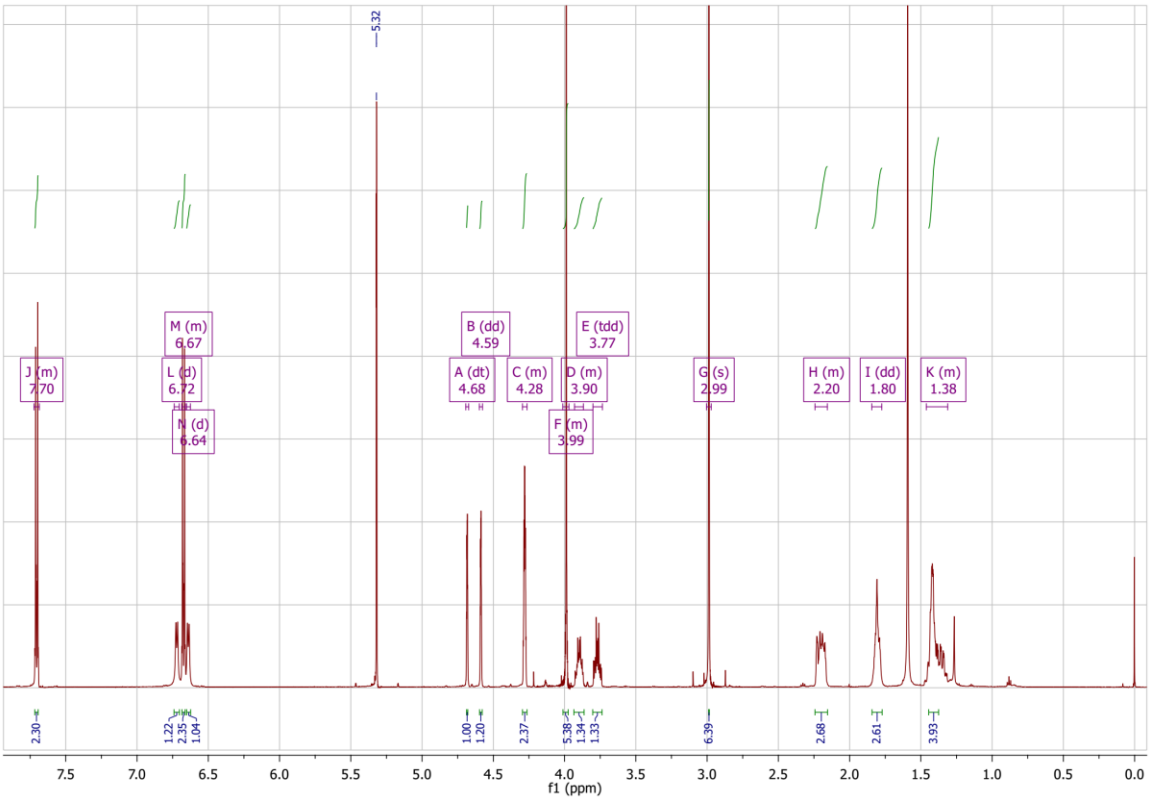
^{1}H NMR (300 MHz, $CDCl_3$)



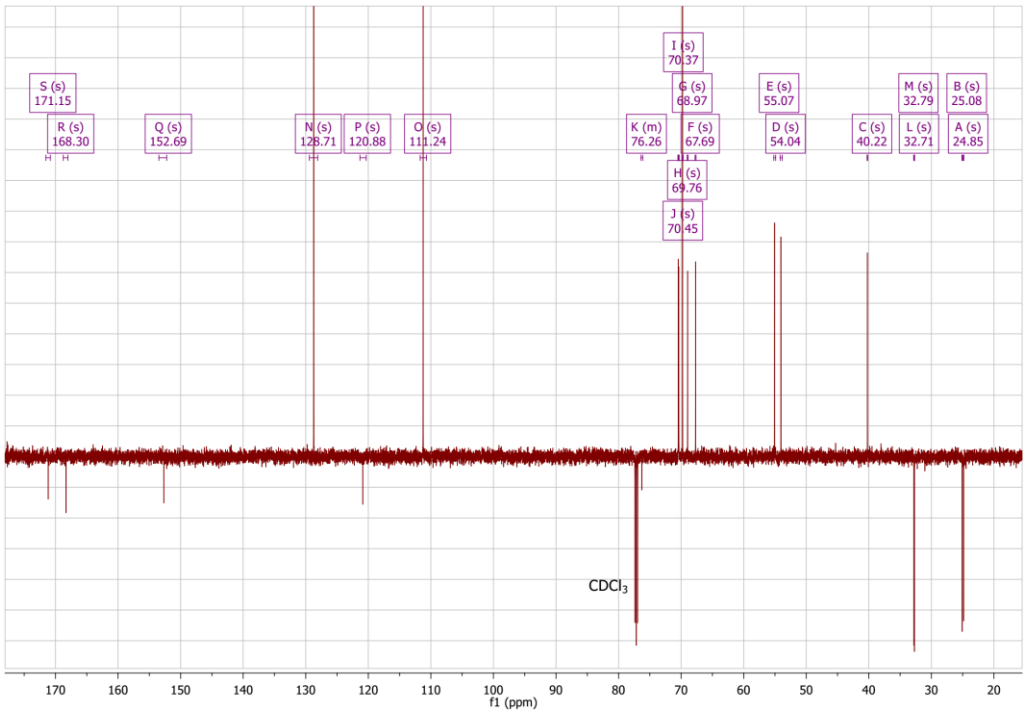


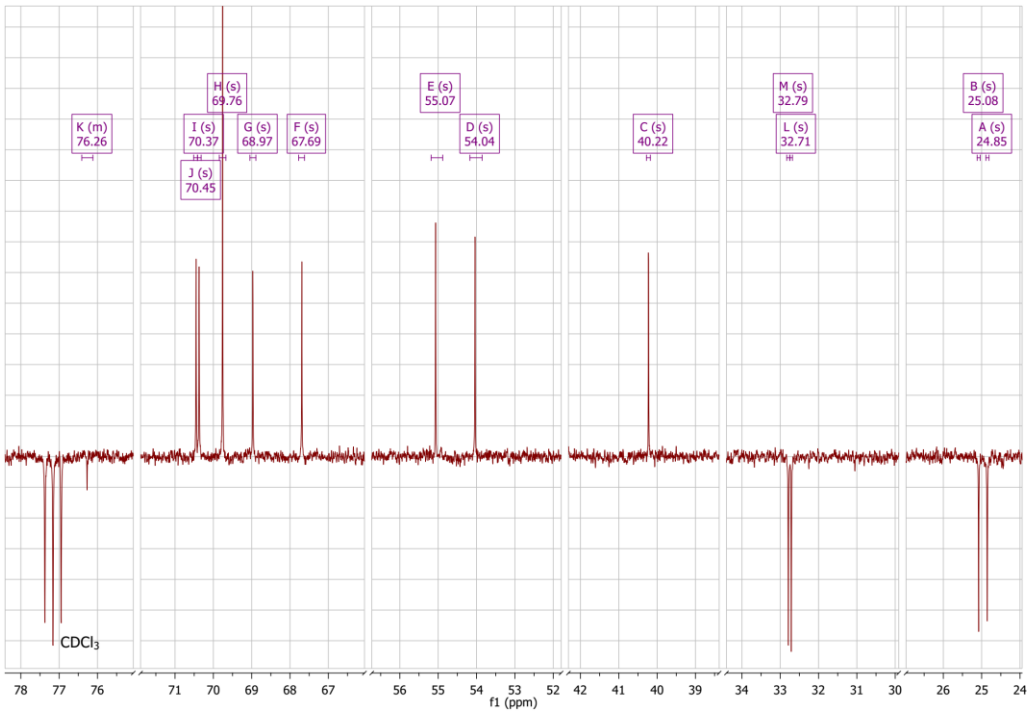


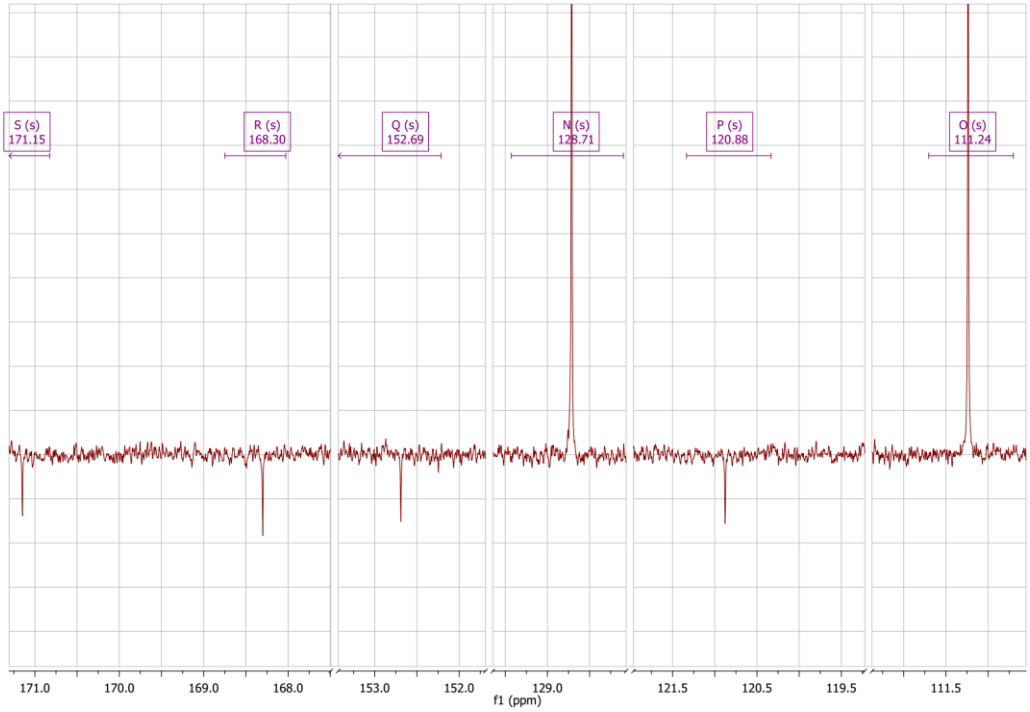
^{1}H NMR (300 MHz, CD_2Cl_2)



^{13}C NMR (151 MHz, $CDCl_3$)

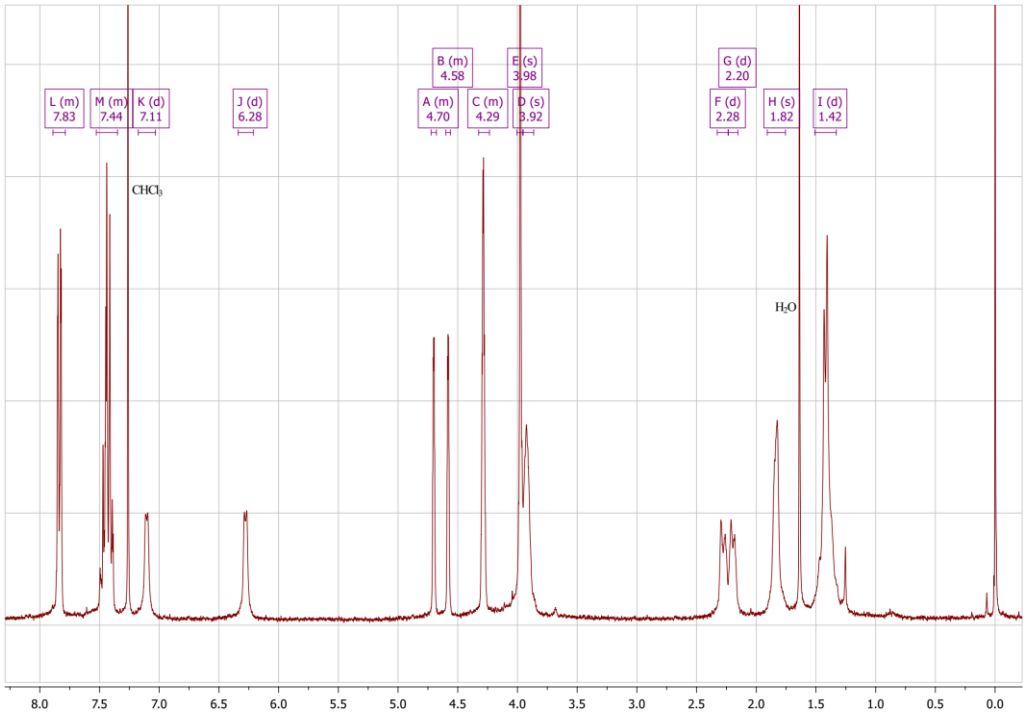


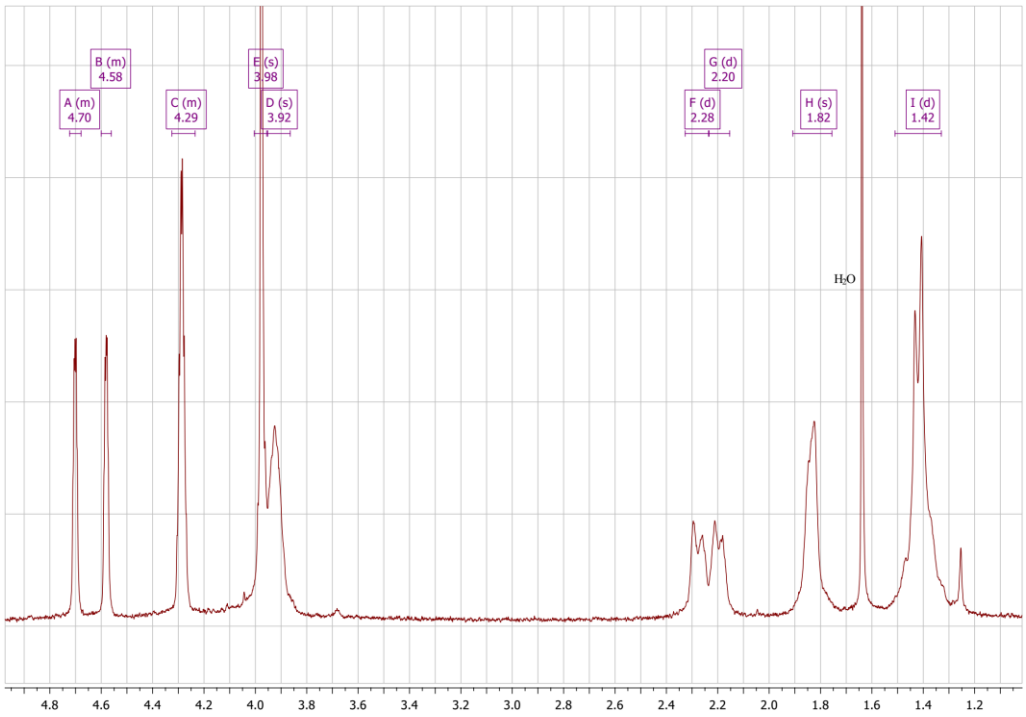

K (m)
76.26
H (s)
69.76
I (s)
70.37
J (s)
70.45
G (s)
68.97
F (s)
67.69
E (s)
55.07
D (s)
54.04
C (s)
40.22
M (s)
32.79
L (s)
32.71
B (s)
25.08
A (s)
24.85
CDCl3
78 77 76 71 70 69 68 67 56 55 54 53 52 42 41 40 39 34 33 32 31 30 26 25 24
f1 (ppm)

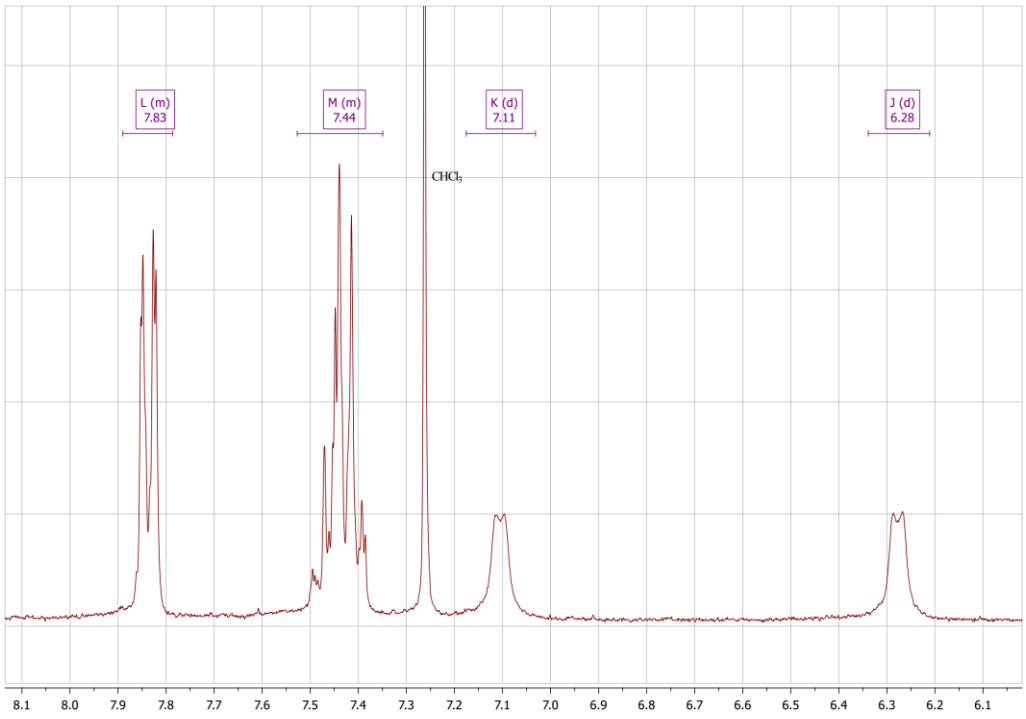

S (s)
171.15
R (s)
168.30
Q (s)
152.69
N (s)
128.71
P (s)
120.88
O (s)
111.24
171.0 170.0 169.0 168.0 153.0 152.0 129.0 121.5 120.5 119.5 111.5
f1 (ppm)

5.4 1b

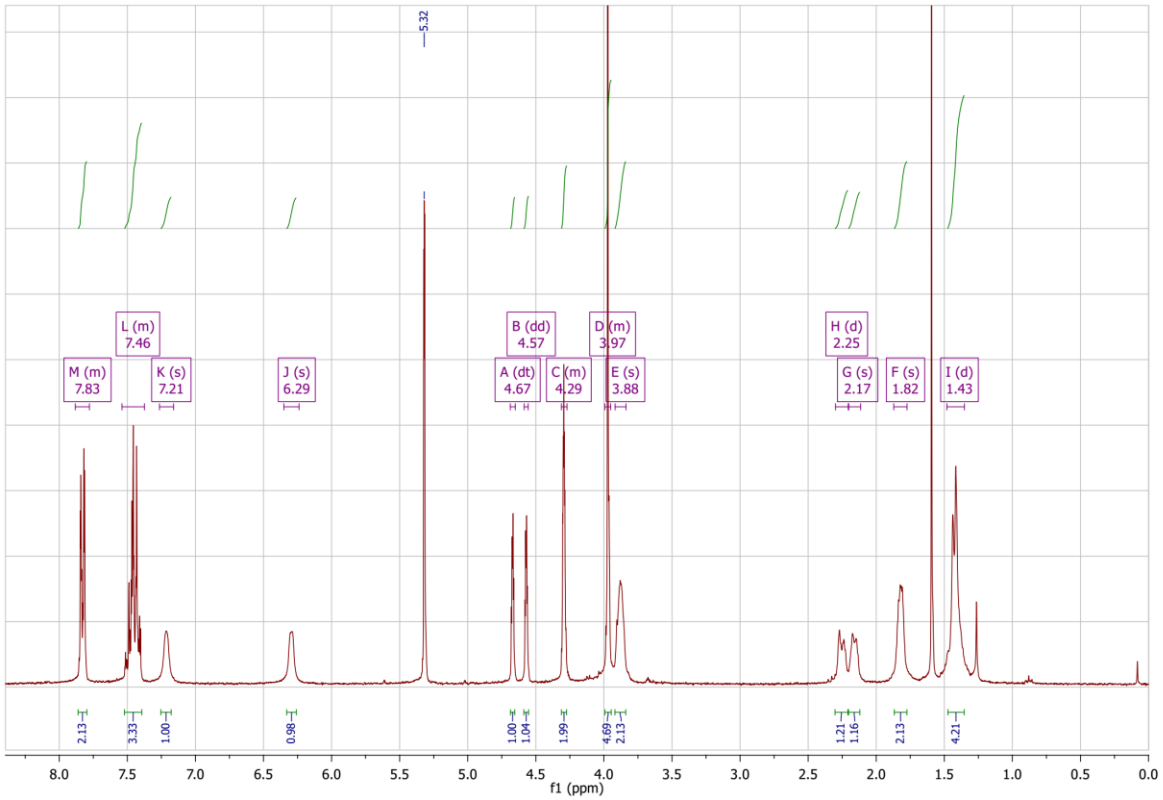
^{1}H NMR (300 MHz, $CDCl_3$)



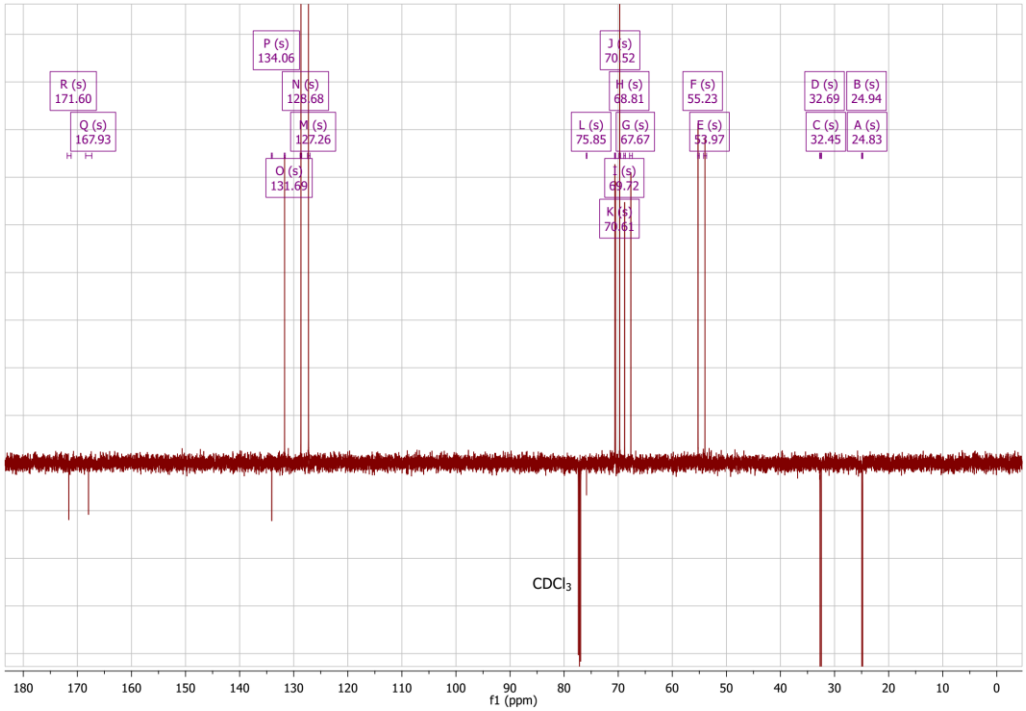


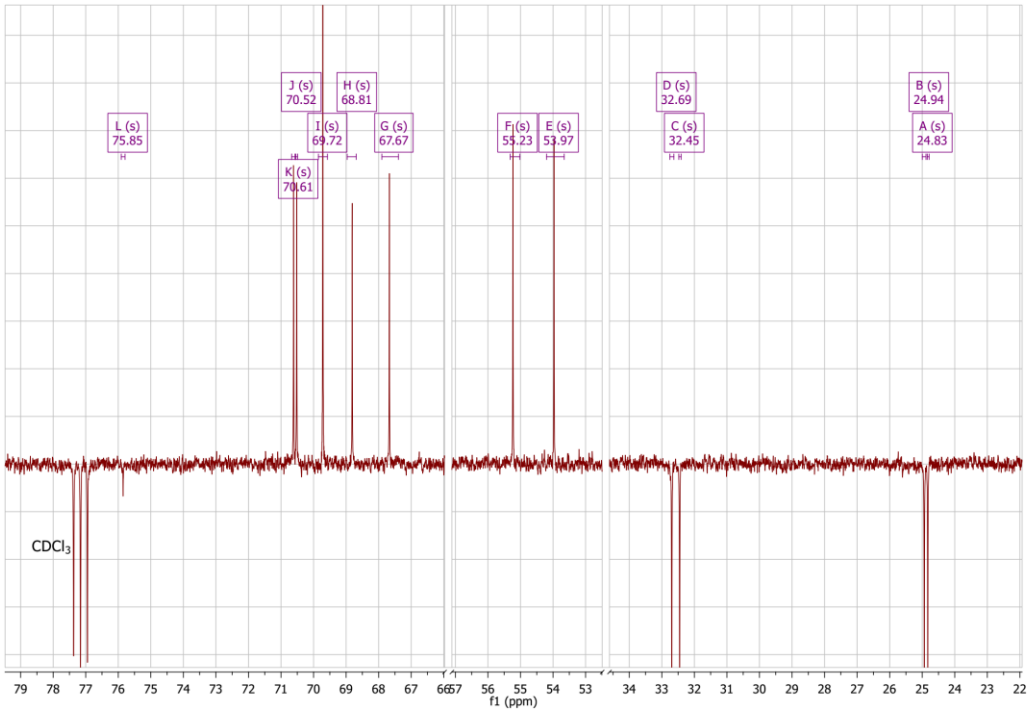


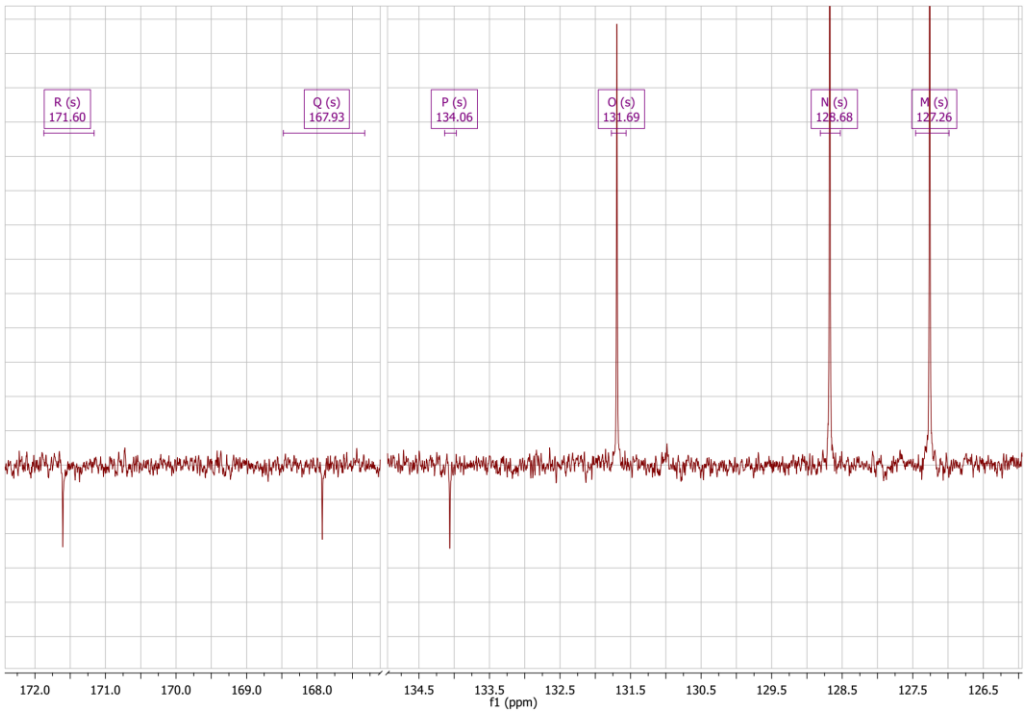
^{1}H NMR (300 MHz, CD_2Cl_2)



^{13}C NMR (151 MHz, $CDCl_3$)

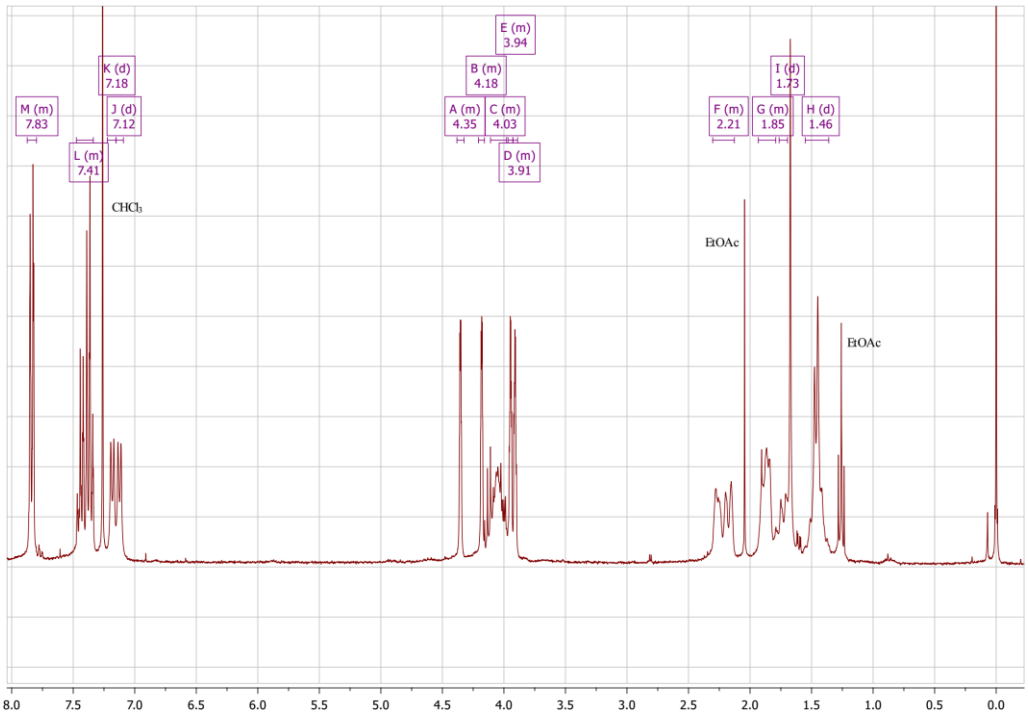


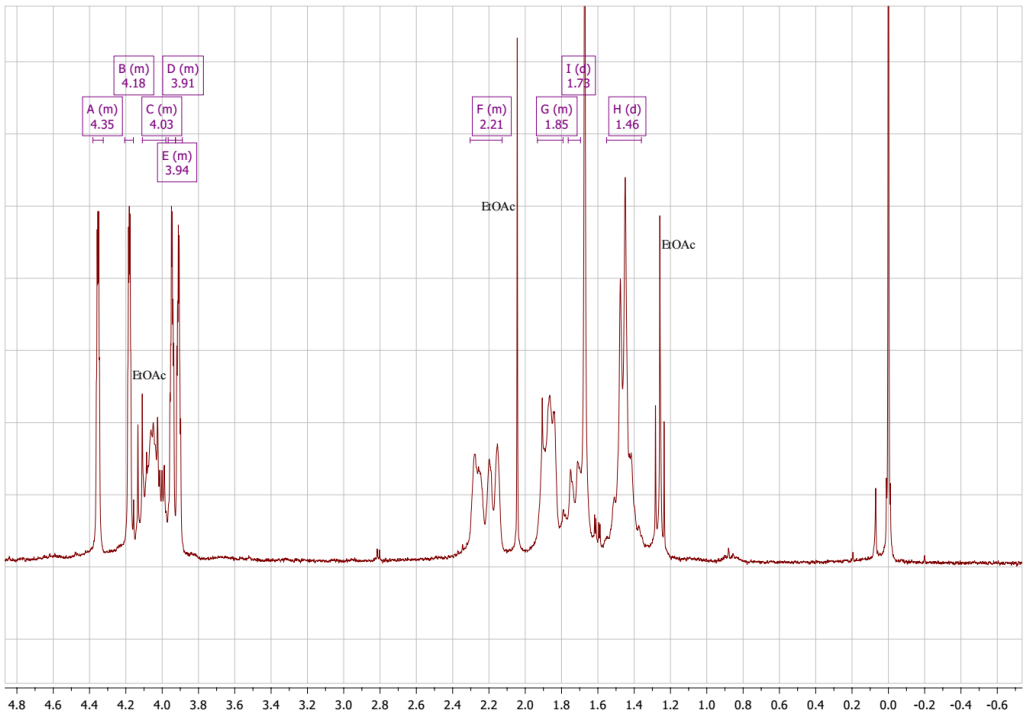


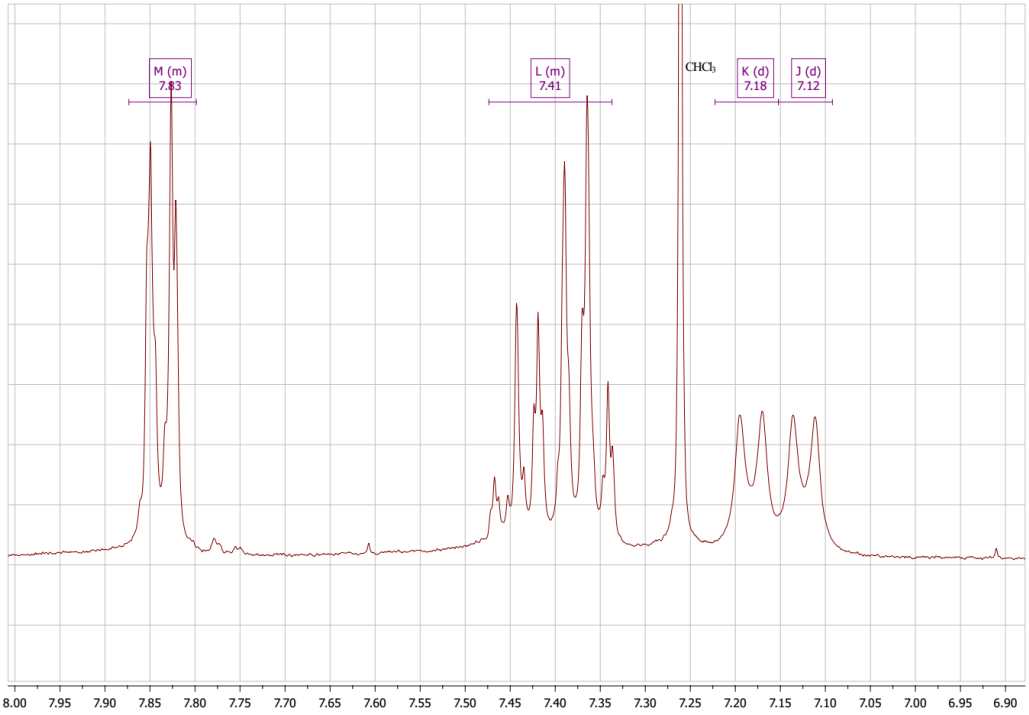


5.5 2b

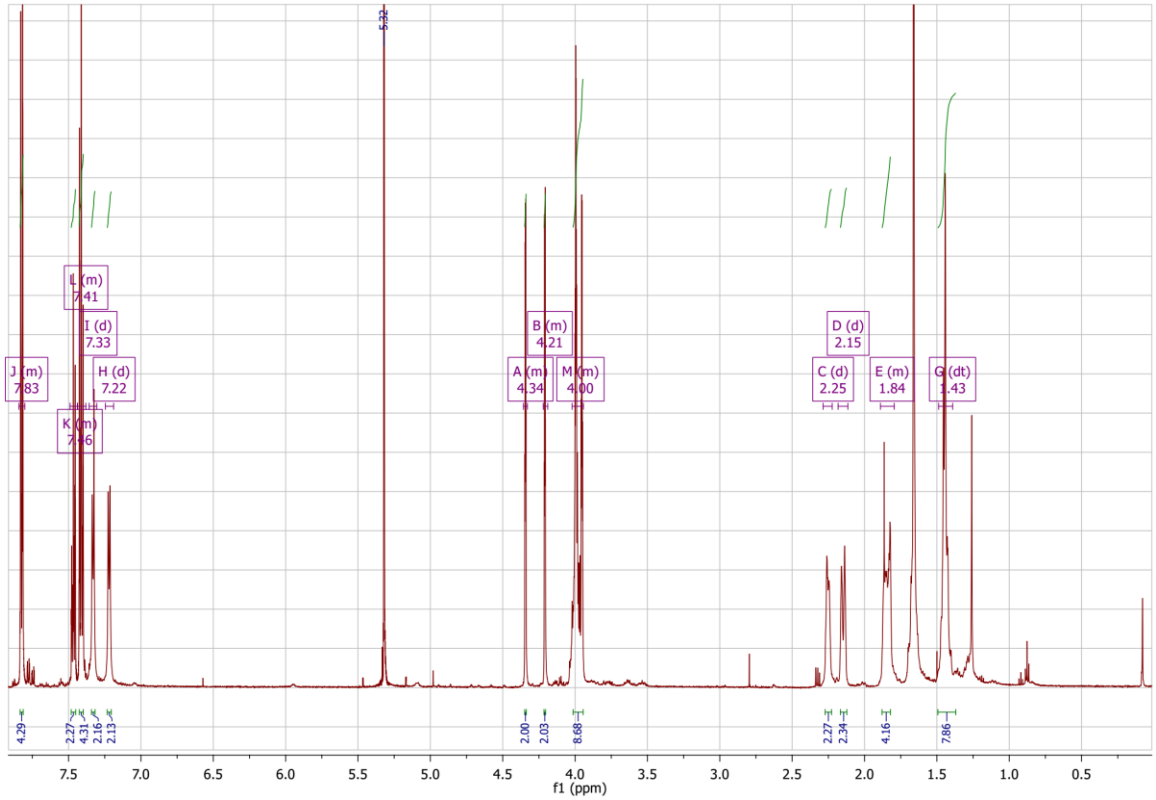
^{1}H NMR (300 MHz, $CDCl_3$)



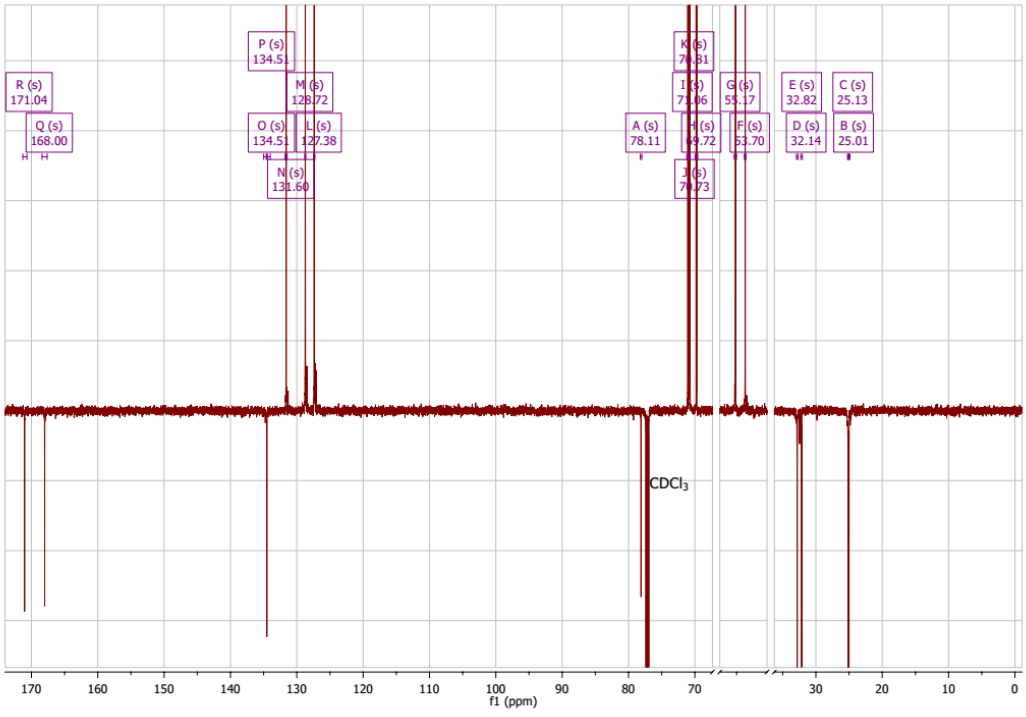

A (m) 4.35
B (m) 4.18
C (m) 4.03
D (m) 3.91
E (m) 3.94
F (m) 2.21
G (m) 1.85
H (d) 1.46
I (d) 1.73
EtOAc
EtOAc
EtOAc
4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 -0.2 -0.4 -0.6

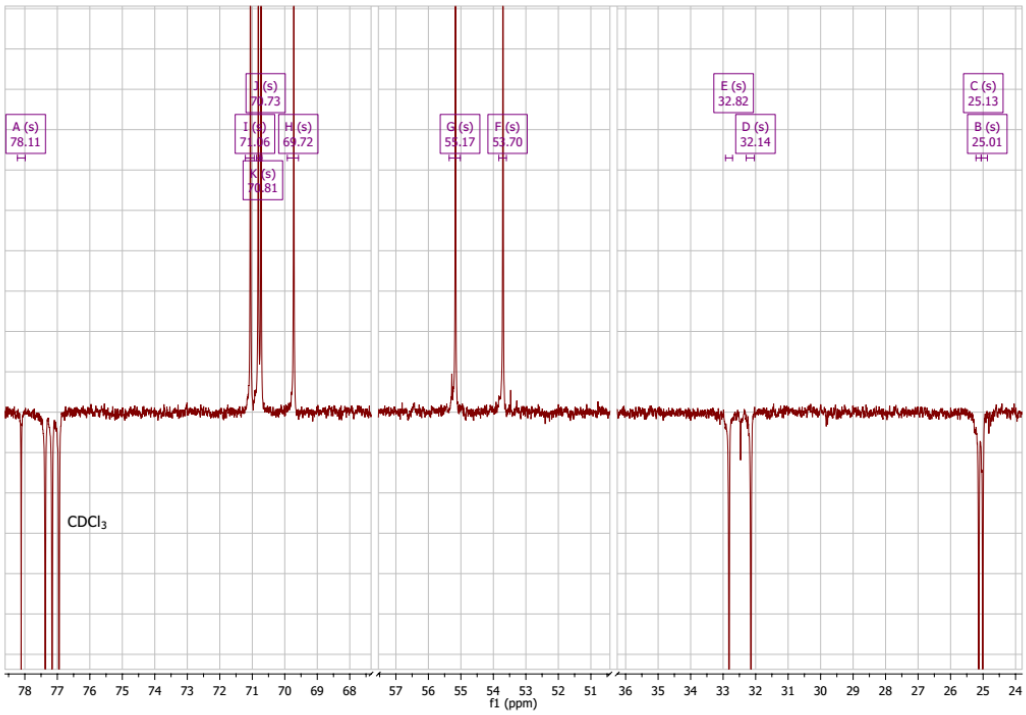

M (m) 7.83
L (m) 7.41
CHCl3
K (d) 7.18
J (d) 7.12
8.00 7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90

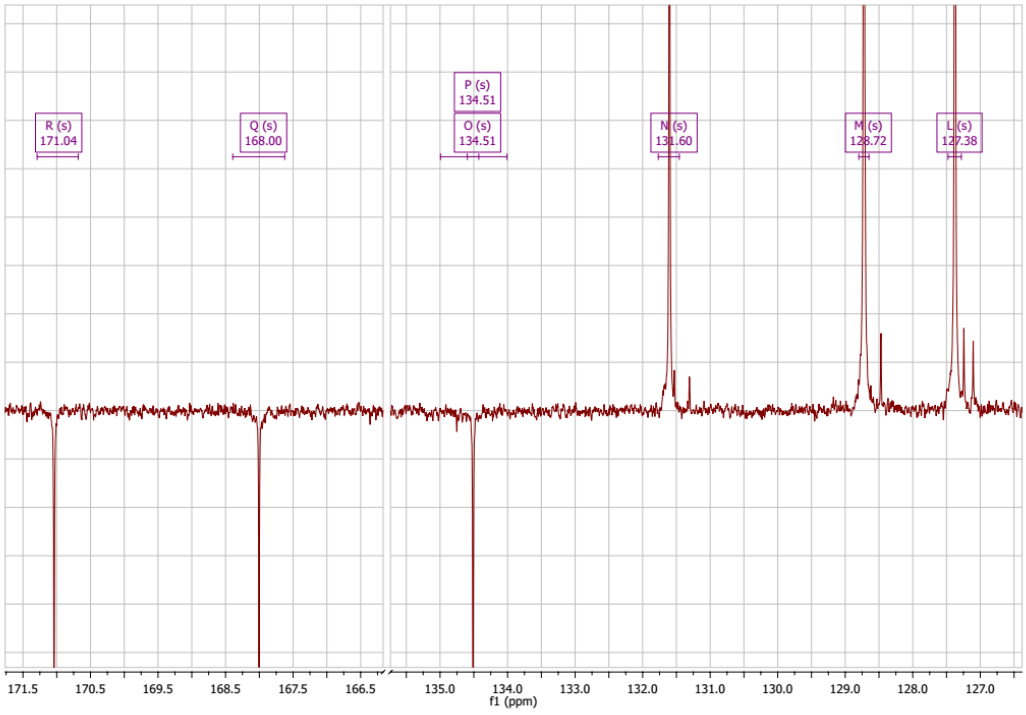
^{1}H NMR (300 MHz, CD_2Cl_2)



^{13}C NMR (151 MHz, $CDCl_3$)

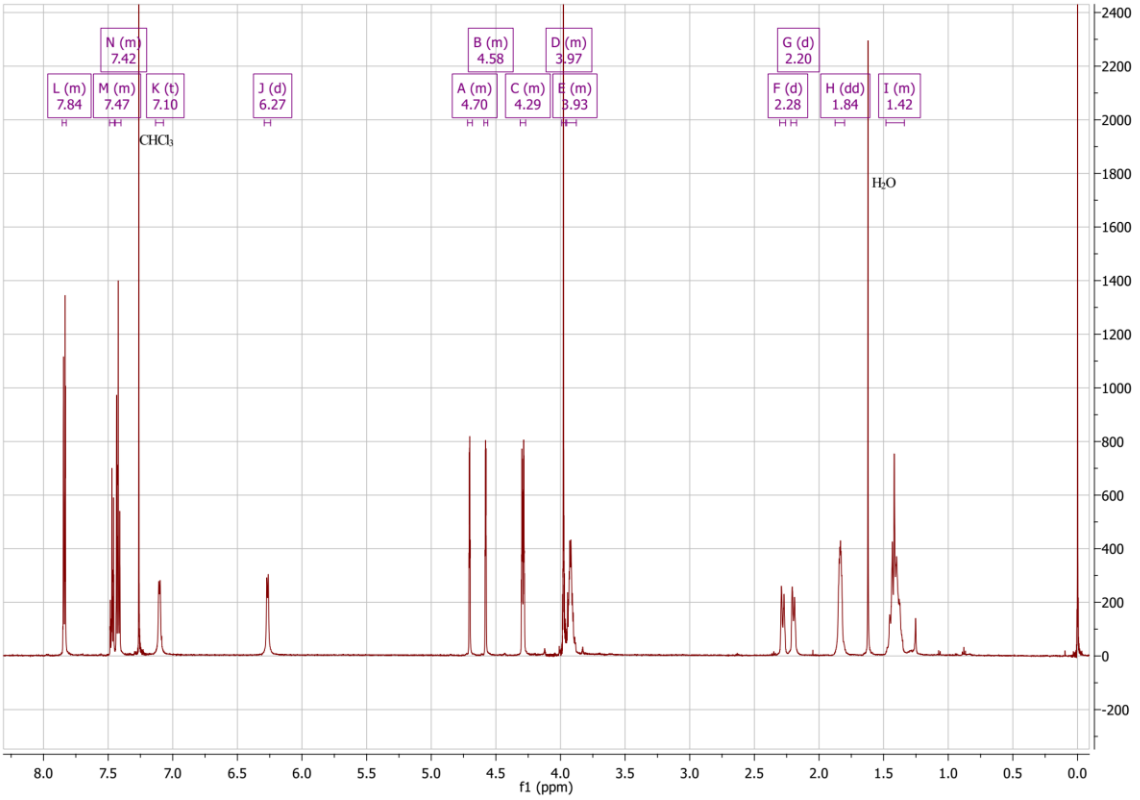


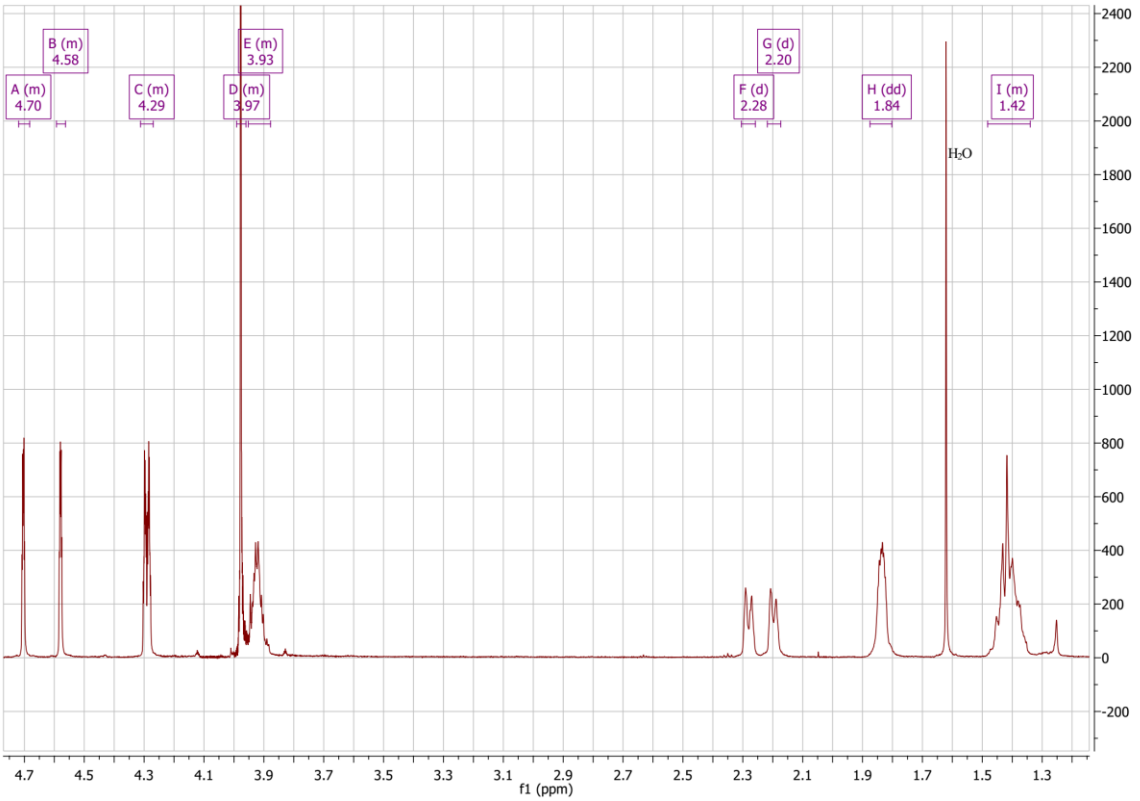

A (s)
78.11
J (s)
70.73
I (s)
71.06
H (s)
69.72
K (s)
70.81
G (s)
55.17
F (s)
53.70
E (s)
32.82
D (s)
32.14
C (s)
25.13
B (s)
25.01
CDCl3
78 77 76 75 74 73 72 71 70 69 68 57 56 55 54 53 52 51 36 35 34 33 32 31 30 29 28 27 26 25 24
f1 (ppm)

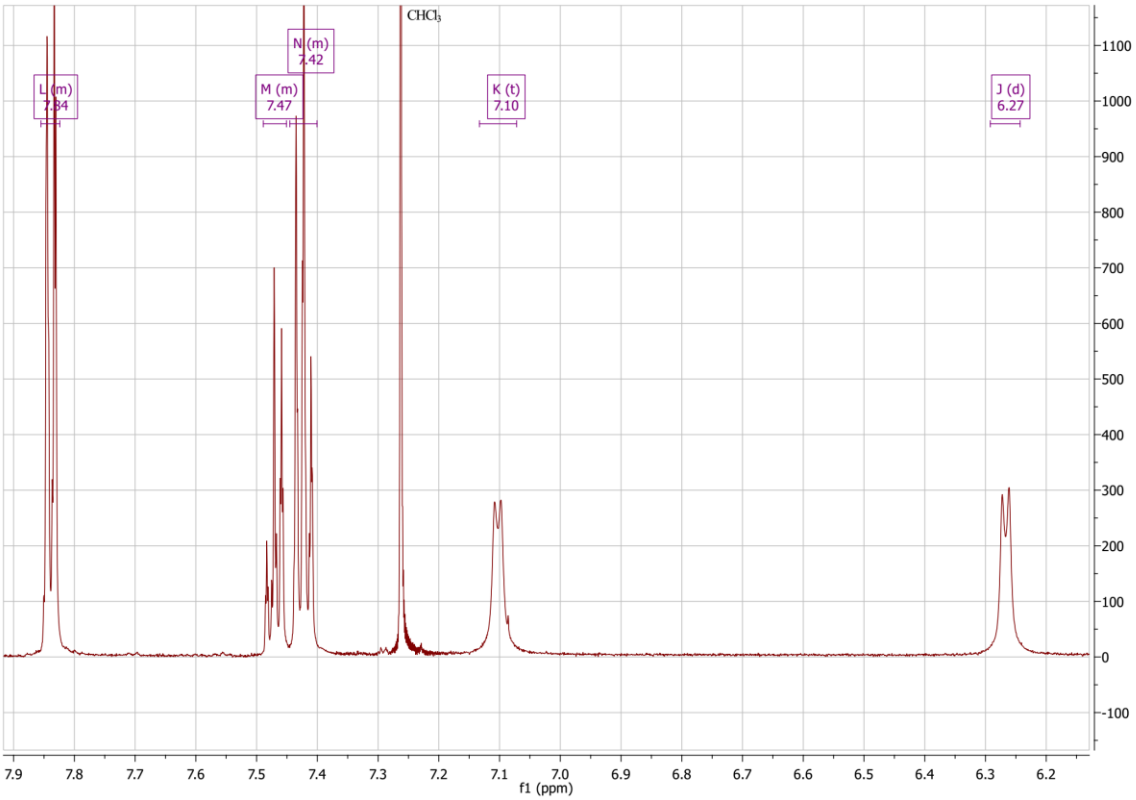

R (s)
171.04
Q (s)
168.00
P (s)
134.51
O (s)
134.51
N (s)
131.60
M (s)
128.72
L (s)
127.38
171.5 170.5 169.5 168.5 167.5 166.5 135.0 134.0 133.0 132.0 131.0 130.0 129.0 128.0 127.0
f1 (ppm)

5.6 1b*

^{1}H NMR (300 MHz, $CDCl_3$)

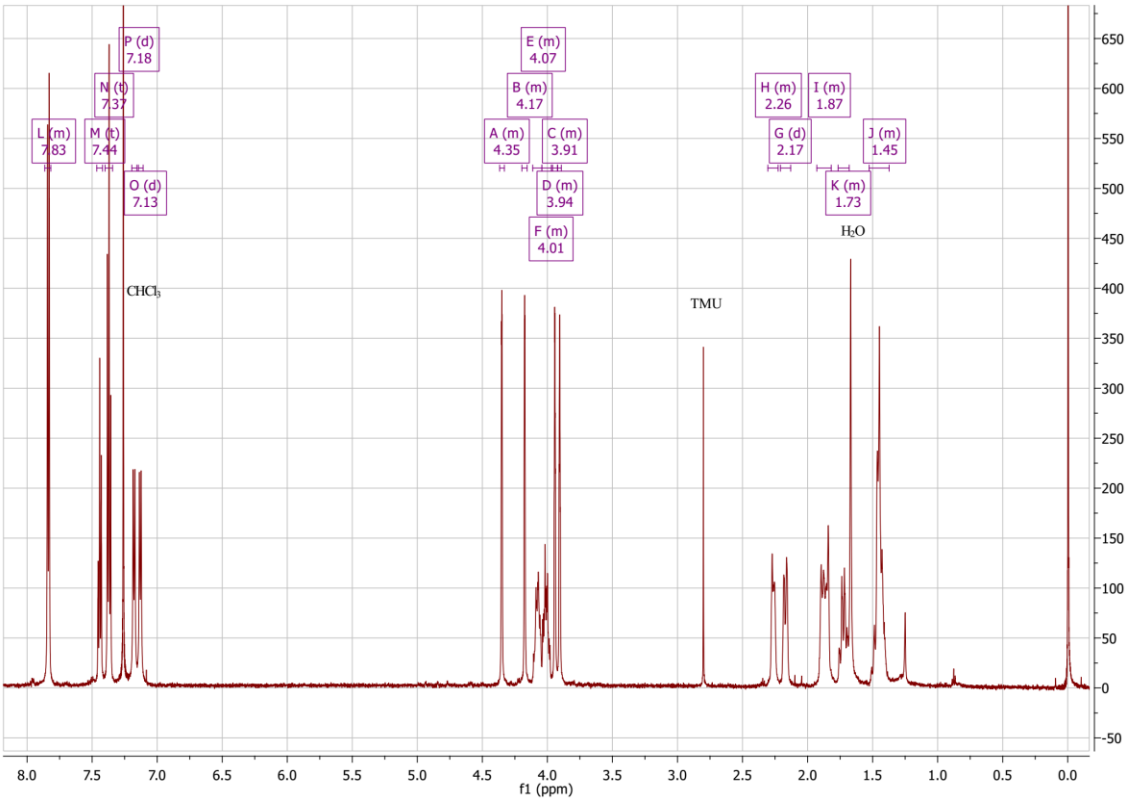


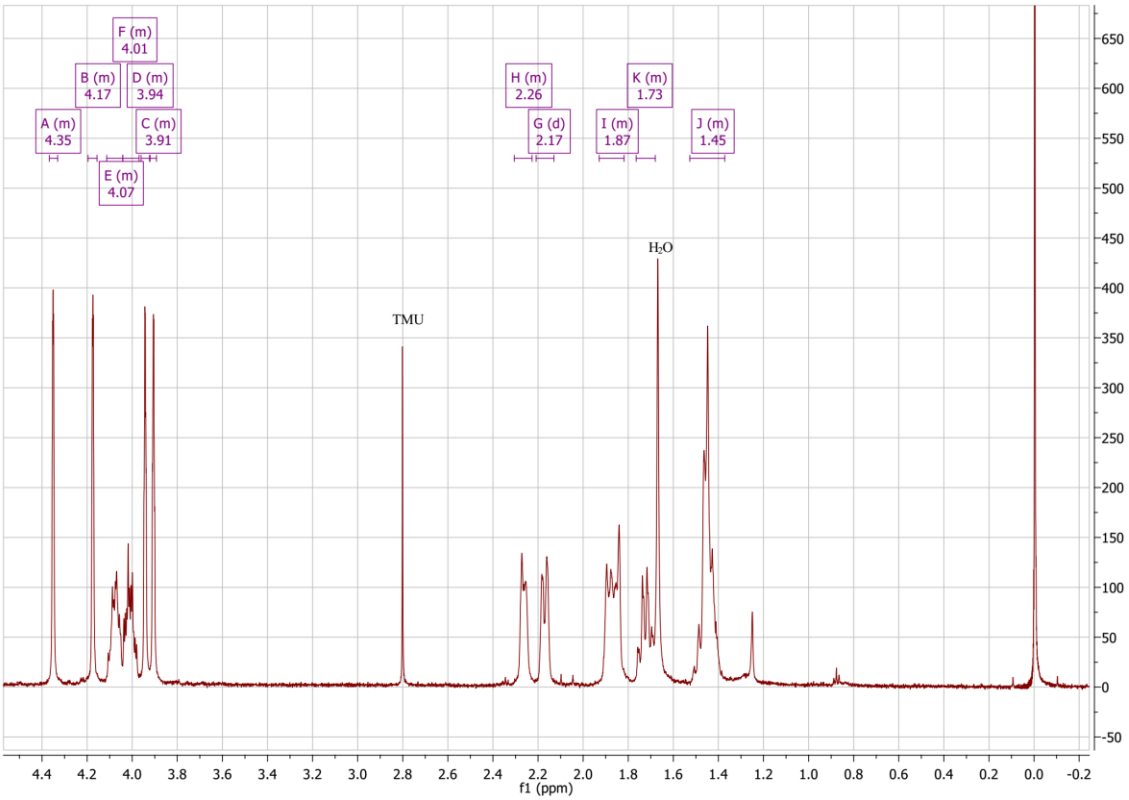


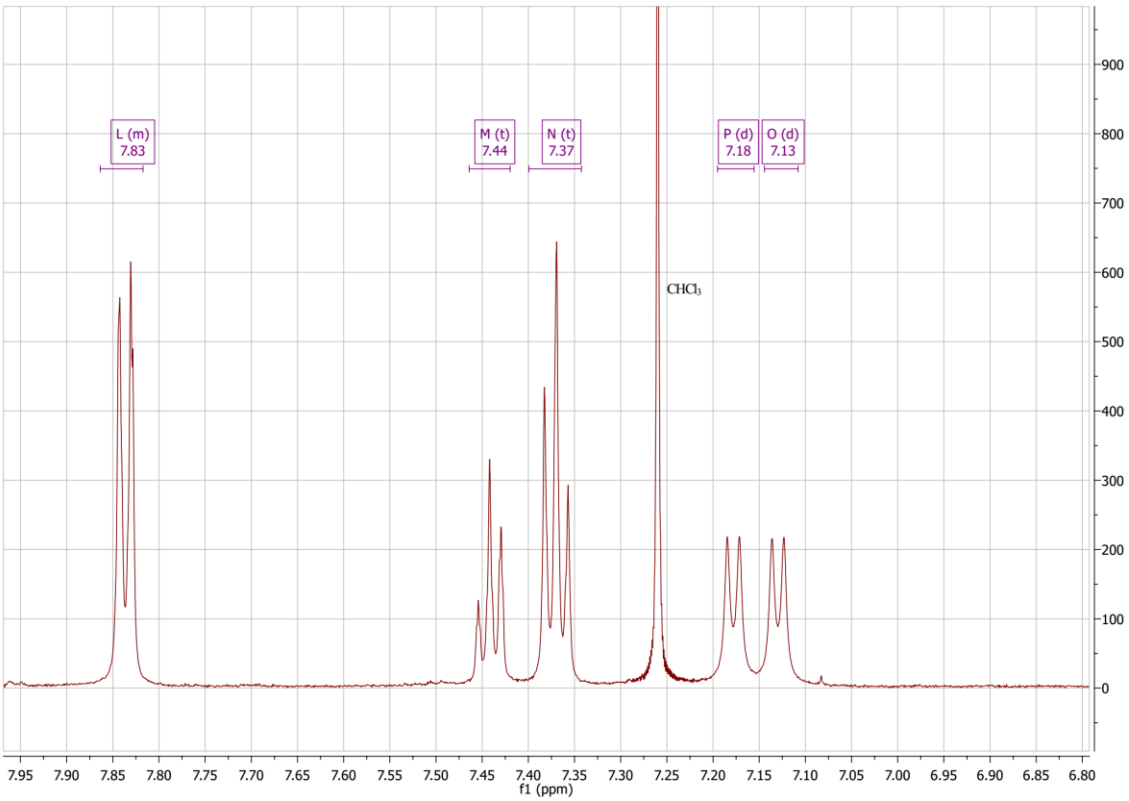


5.7 2b*

^{1}H NMR (300 MHz, $CDCl_3$)

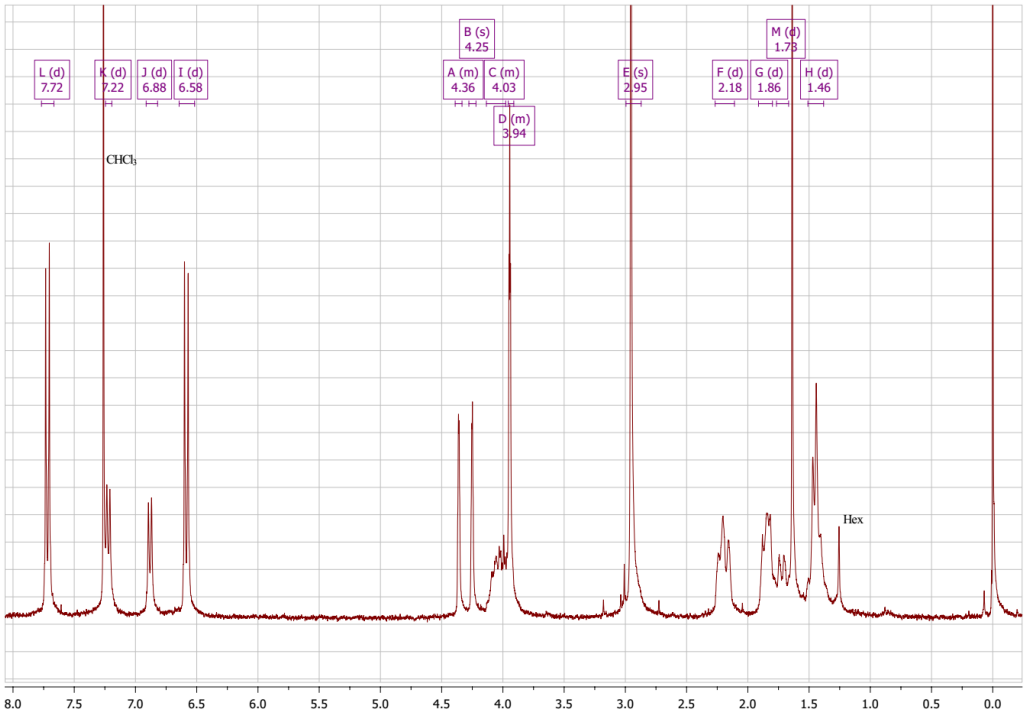


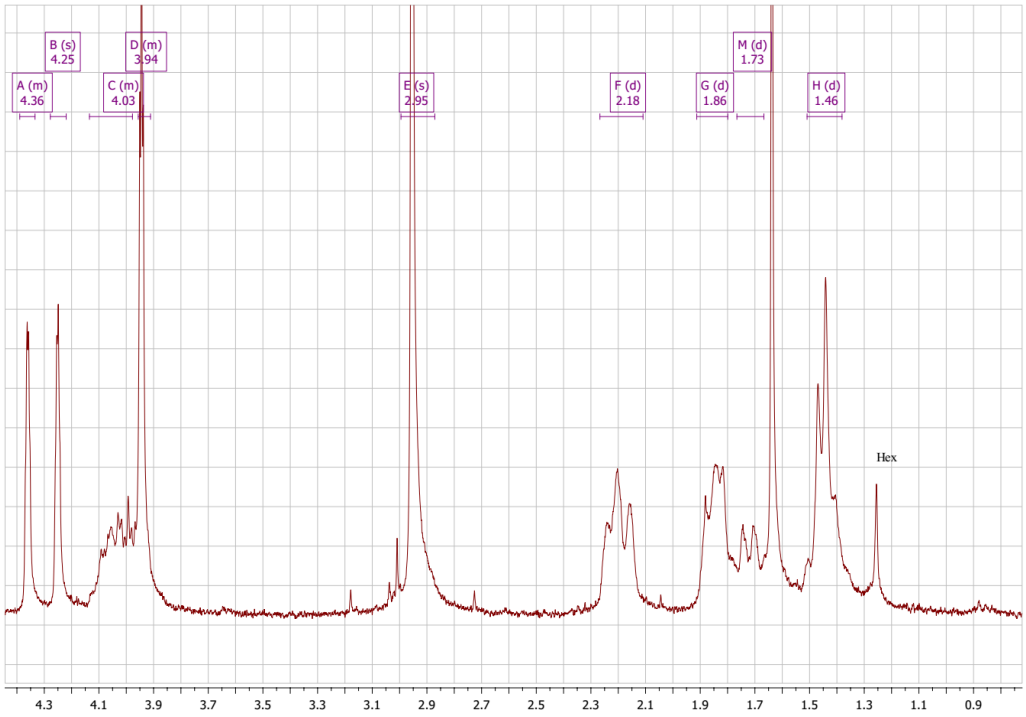

F (m)
4.01
B (m)
4.17
D (m)
3.94
A (m)
4.35
C (m)
3.91
E (m)
4.07
H (m)
2.26
G (d)
2.17
K (m)
1.73
I (m)
1.87
J (m)
1.45
H2O
TMU
f1 (ppm)

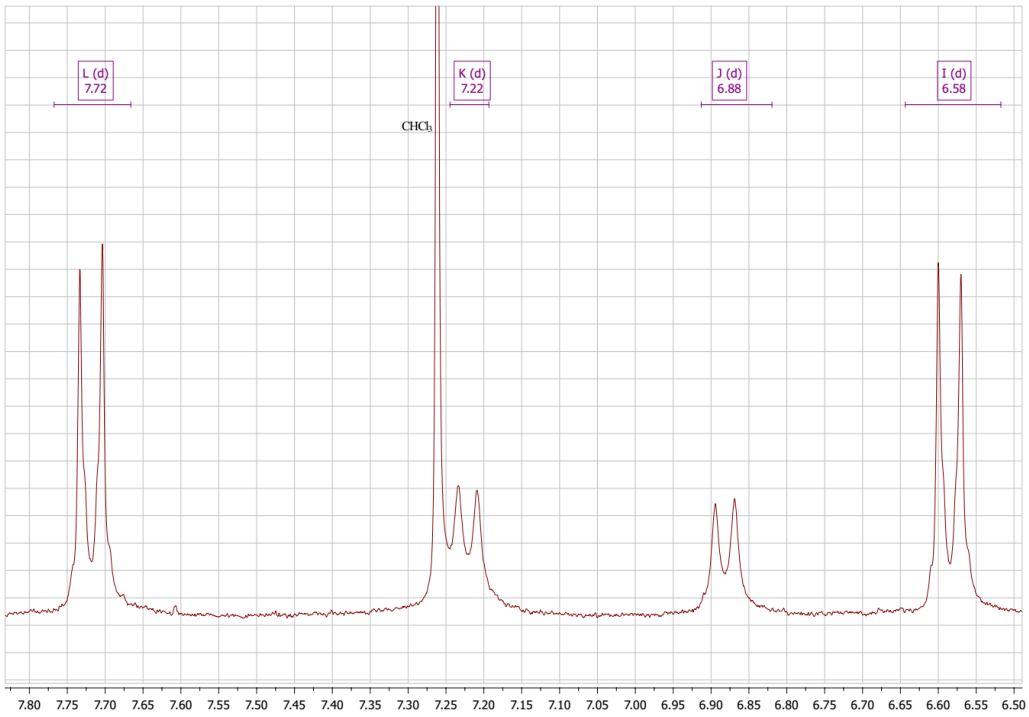

L (m)
7.83
M (t)
7.44
N (t)
7.37
P (d)
7.18
O (d)
7.13
CHCl3
f1 (ppm)

5.8 2n

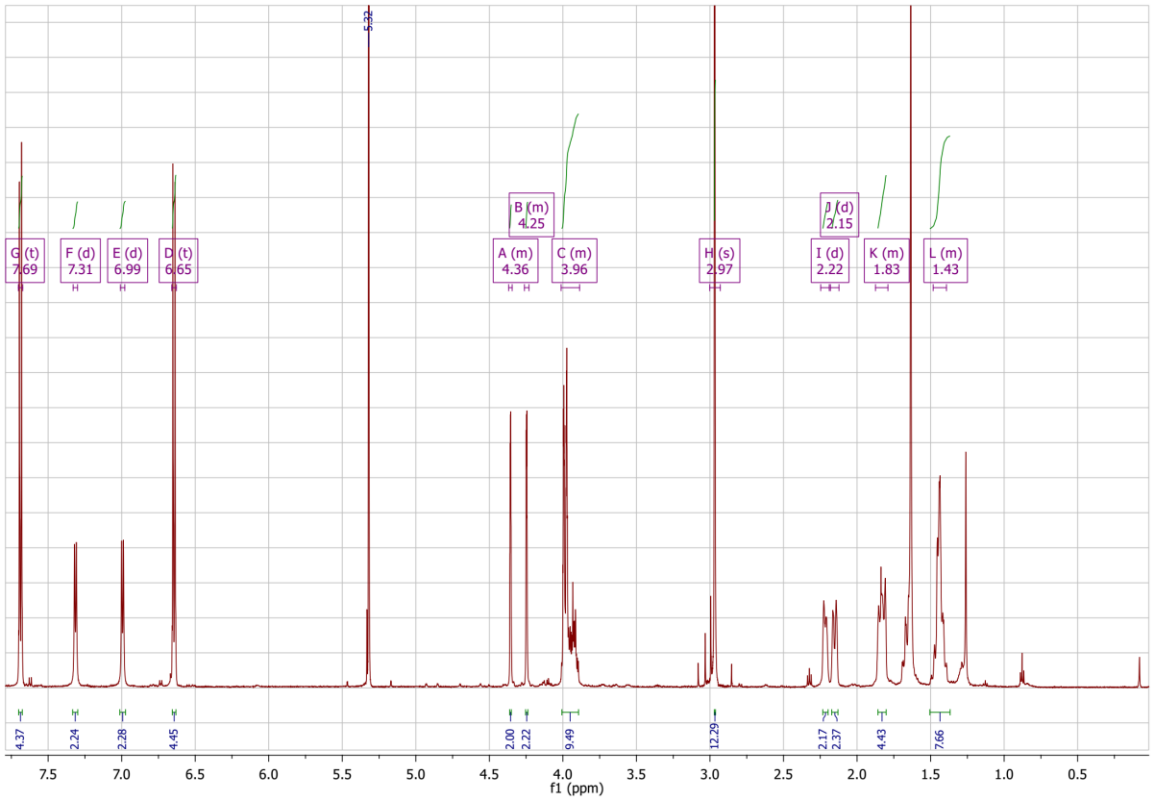
^{1}H NMR (300 MHz, $CDCl_3$)



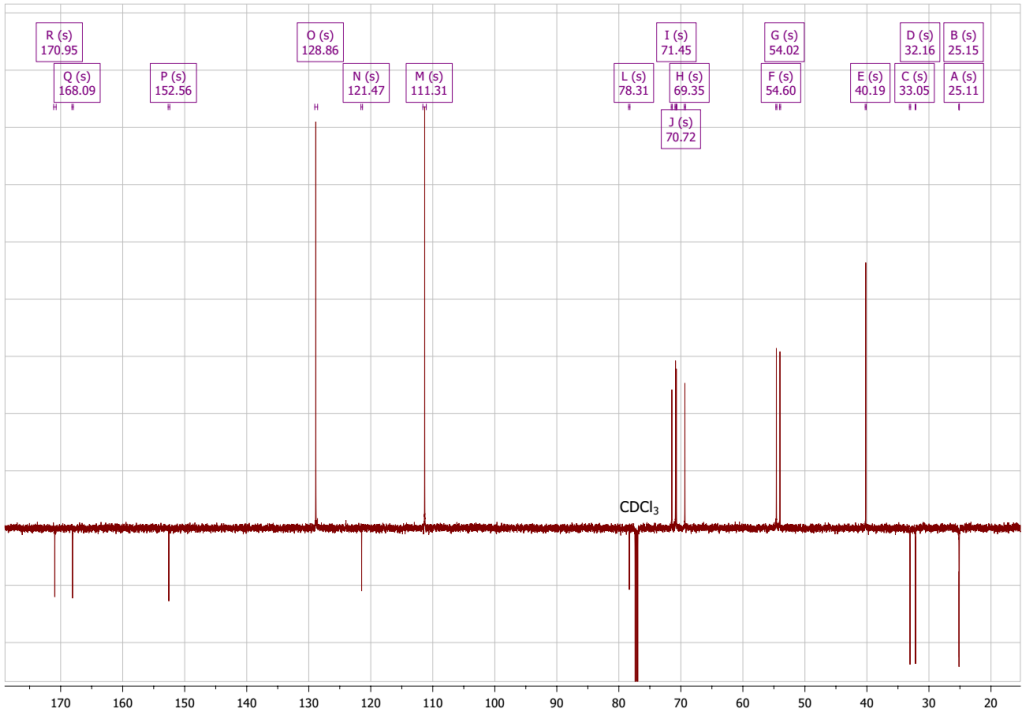


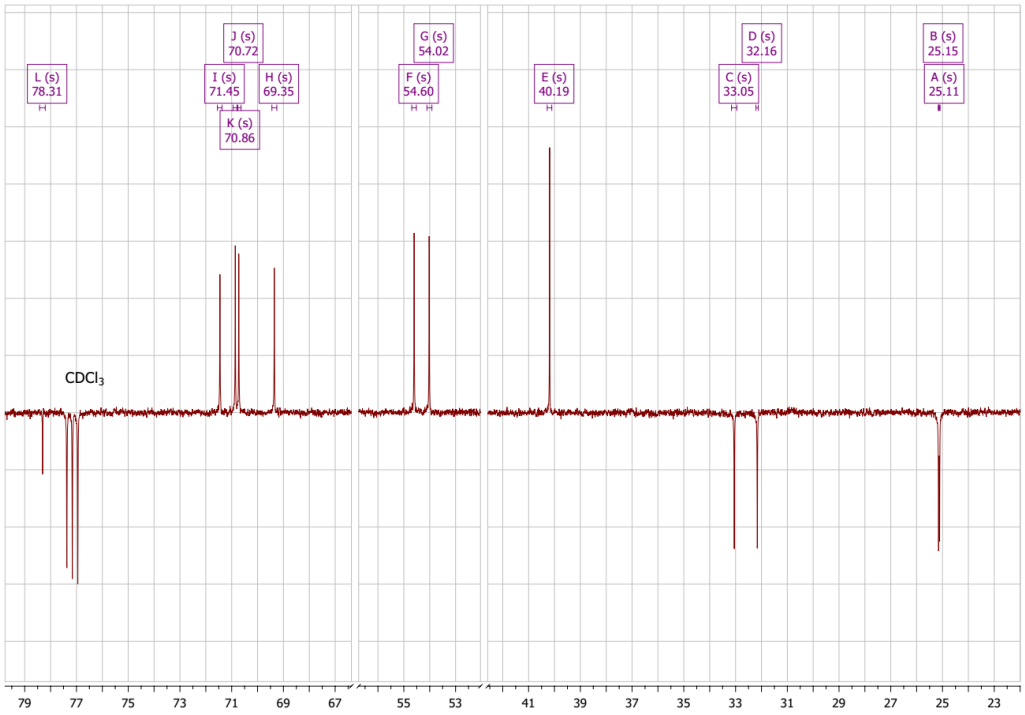


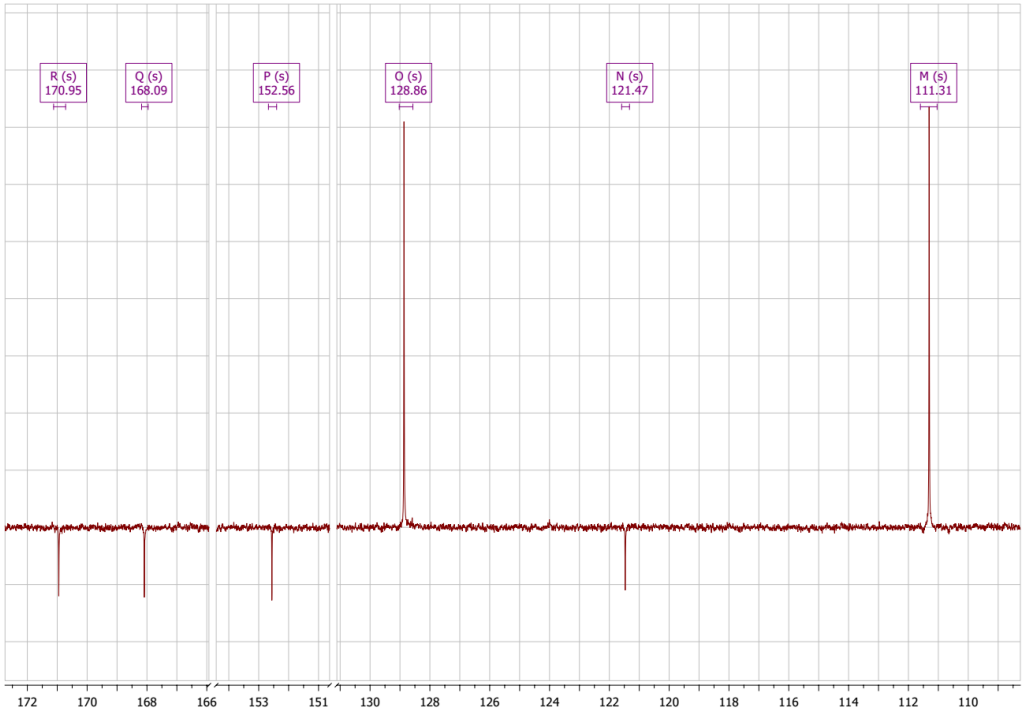
^{1}H NMR (300 MHz, CD_2Cl_2)



^{13}C NMR (151 MHz, $CDCl_3$)

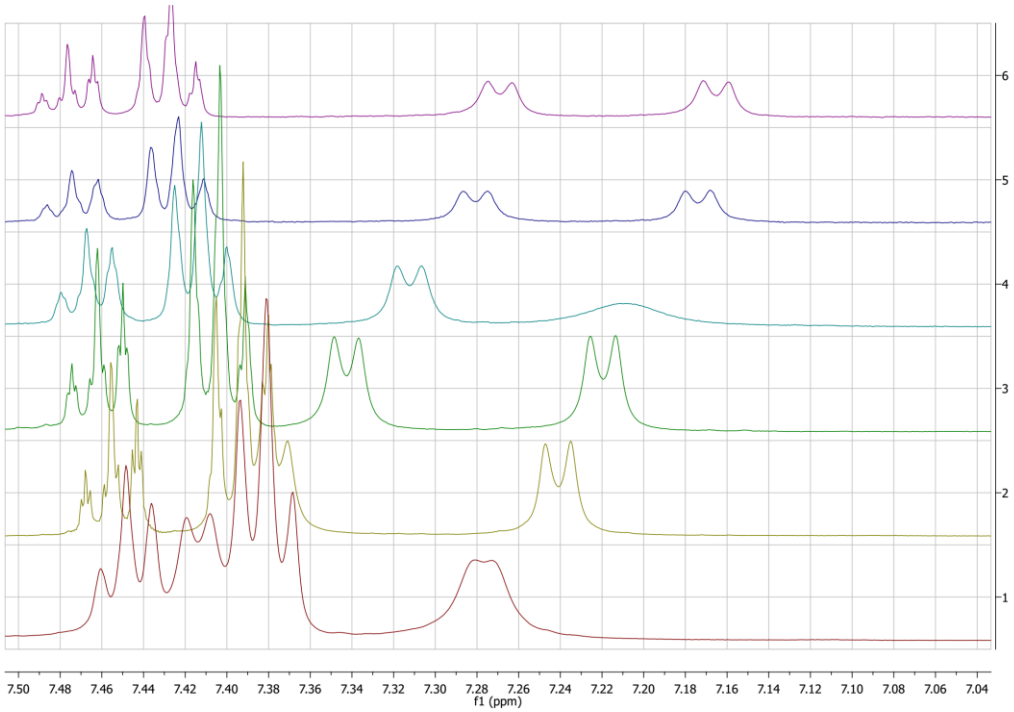





R (s)
170.95
Q (s)
168.09
P (s)
152.56
O (s)
128.86
N (s)
121.47
M (s)
111.31
172
170
168
166
153
151
130
128
126
124
122
120
118
116
114
112
110

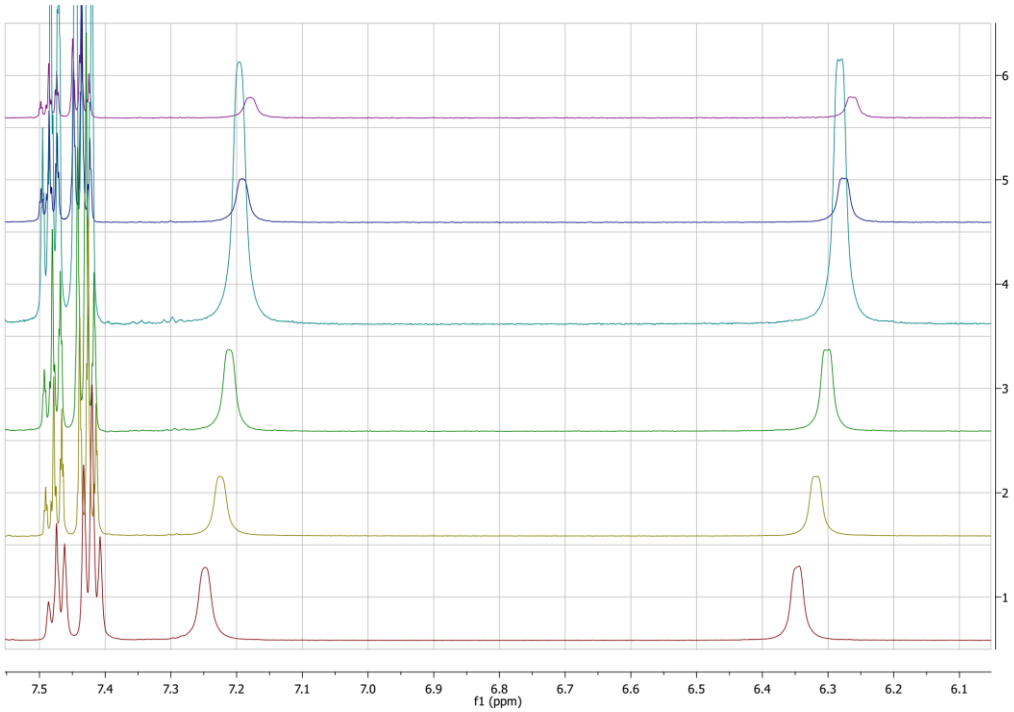
6 Concentration ^{1}H NMR spectra

6.1 2b DCM



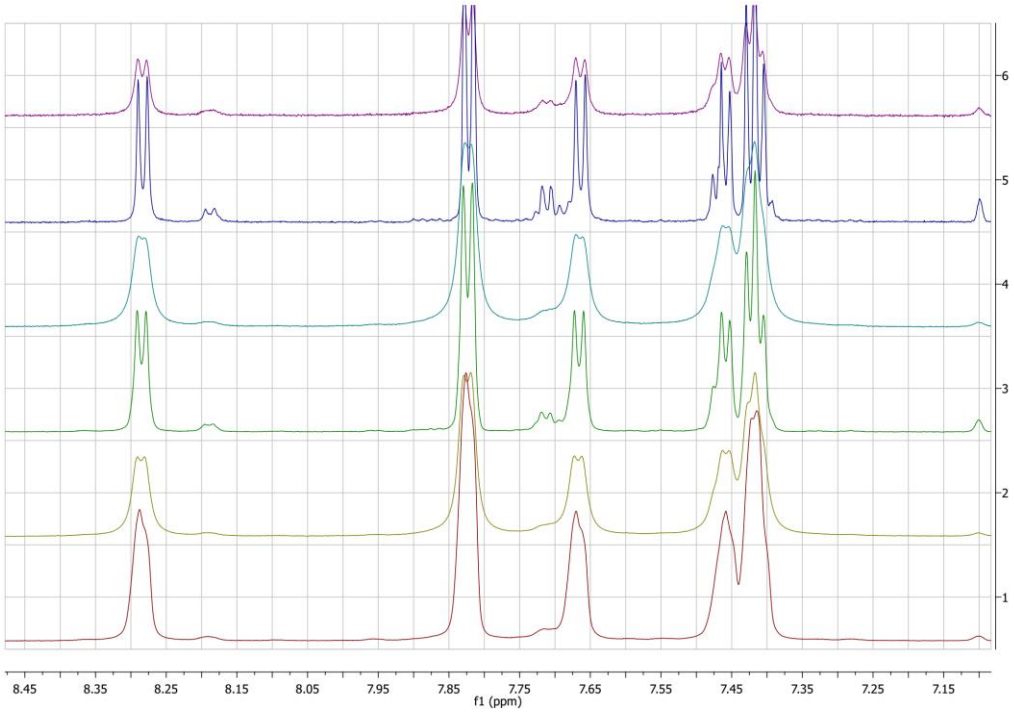
Concentrations from top to bottom in mM =1.52, 3.66, 8.56, 18.12, 28.13, 38.02.

6.2 1b DCM



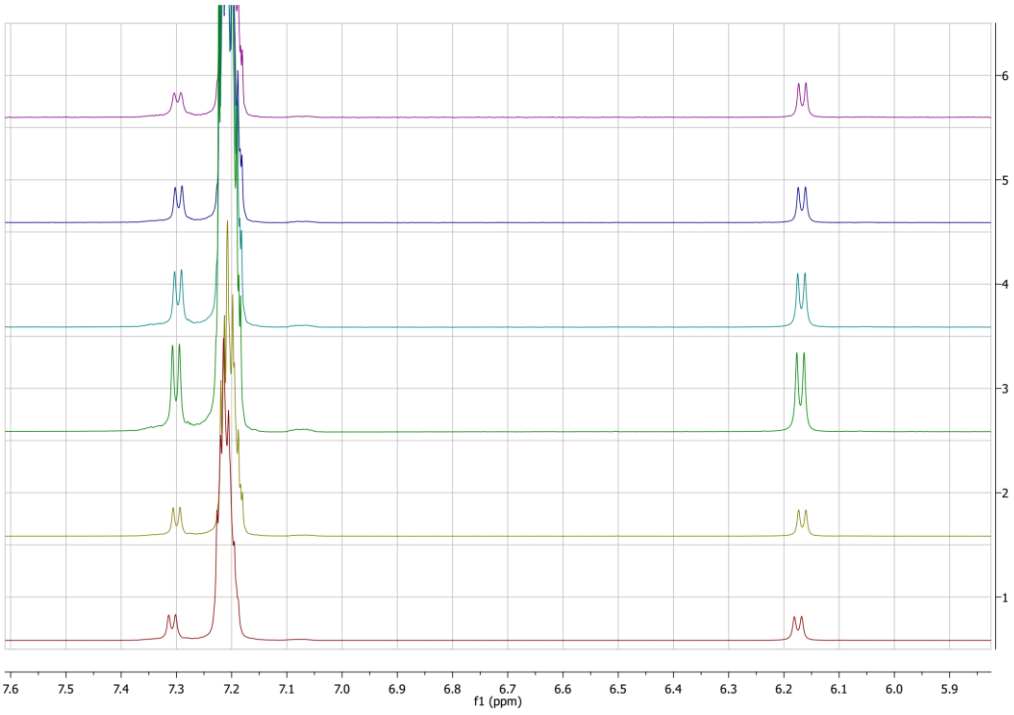
Concentrations from top to bottom in mM = 4.99, 9.76, 13.13, 22.19, 36.14, 50.46.

6.3 2b DMSO



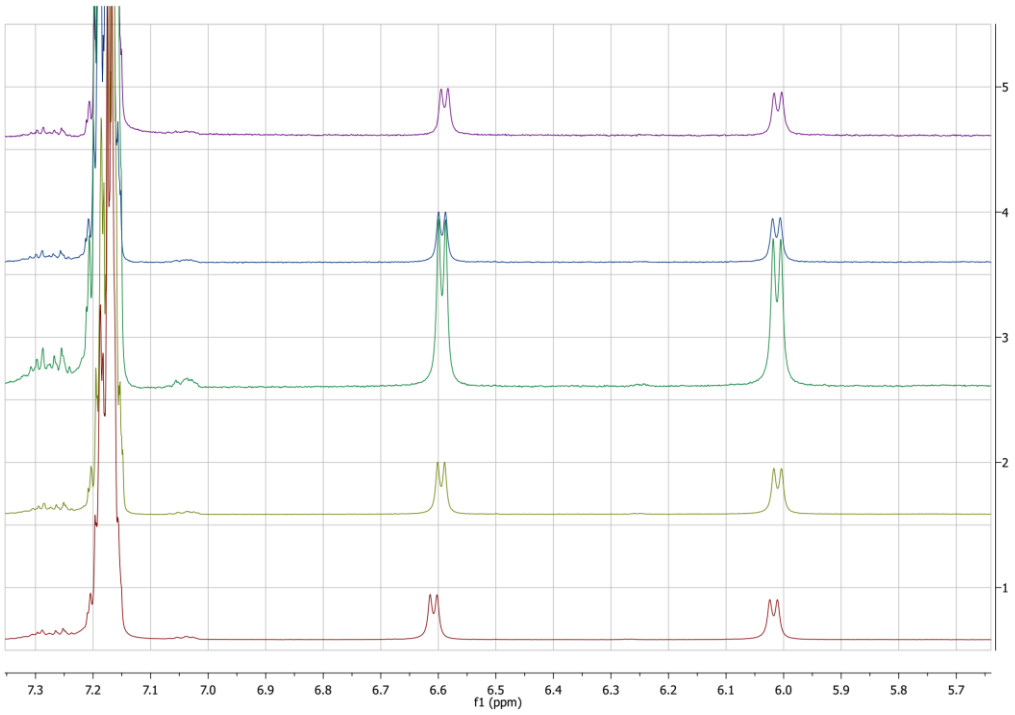
Concentrations from top to bottom in mM = 1.81, 4.78, 12.15, 16.13, 24.35, 31.89.

6.4 2t DCM



Concentrations from top to bottom in mM =1.51, 3.80, 7.60, 14.70, 19.88, 25.74.

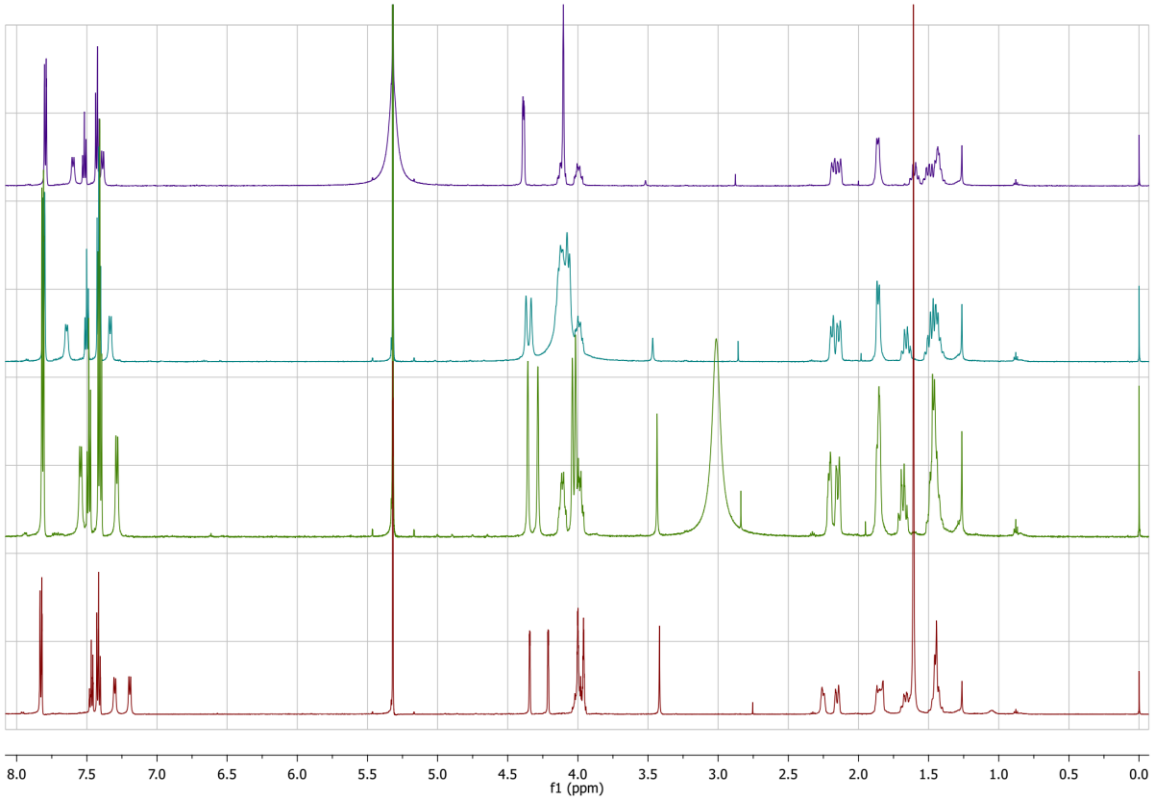
6.5 1t DCM



Concentrations from top to bottom in mM =2.39, 4.57, 8.09, 17.68, 33.74.

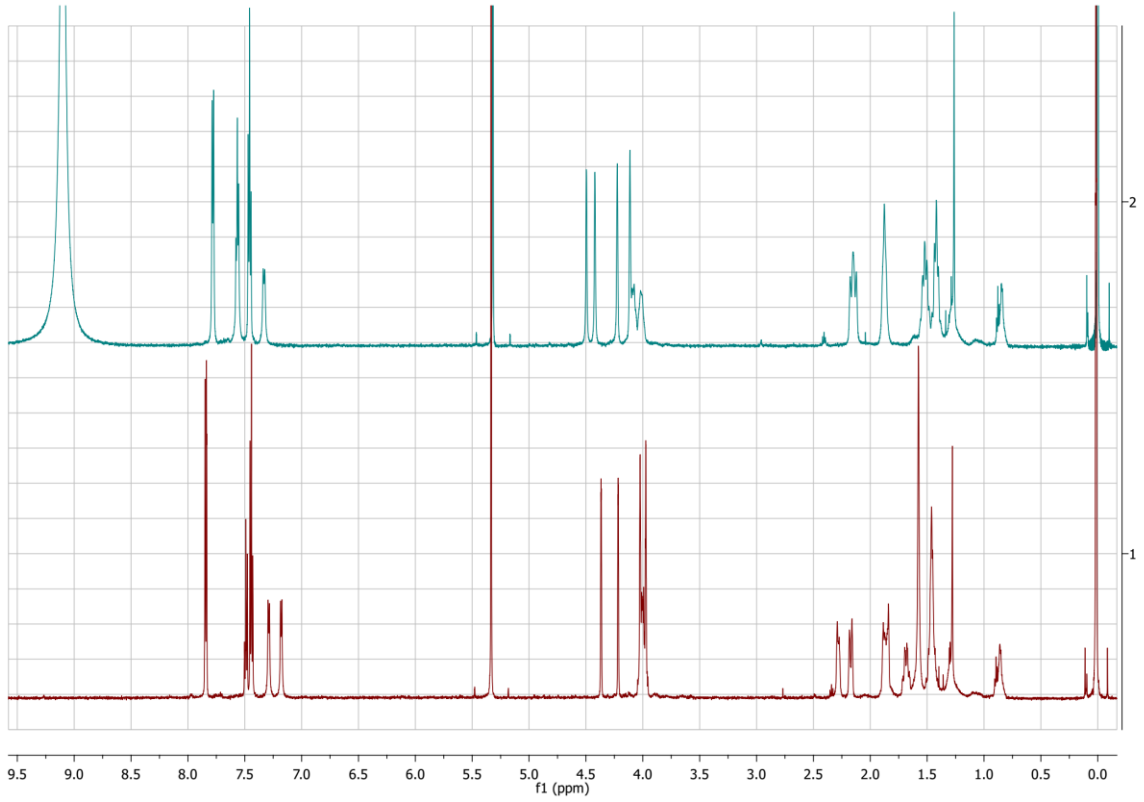
7 ^{1}H NMR 2b + TFA

7.1 2b + 2, 4, 8 eq. TFA



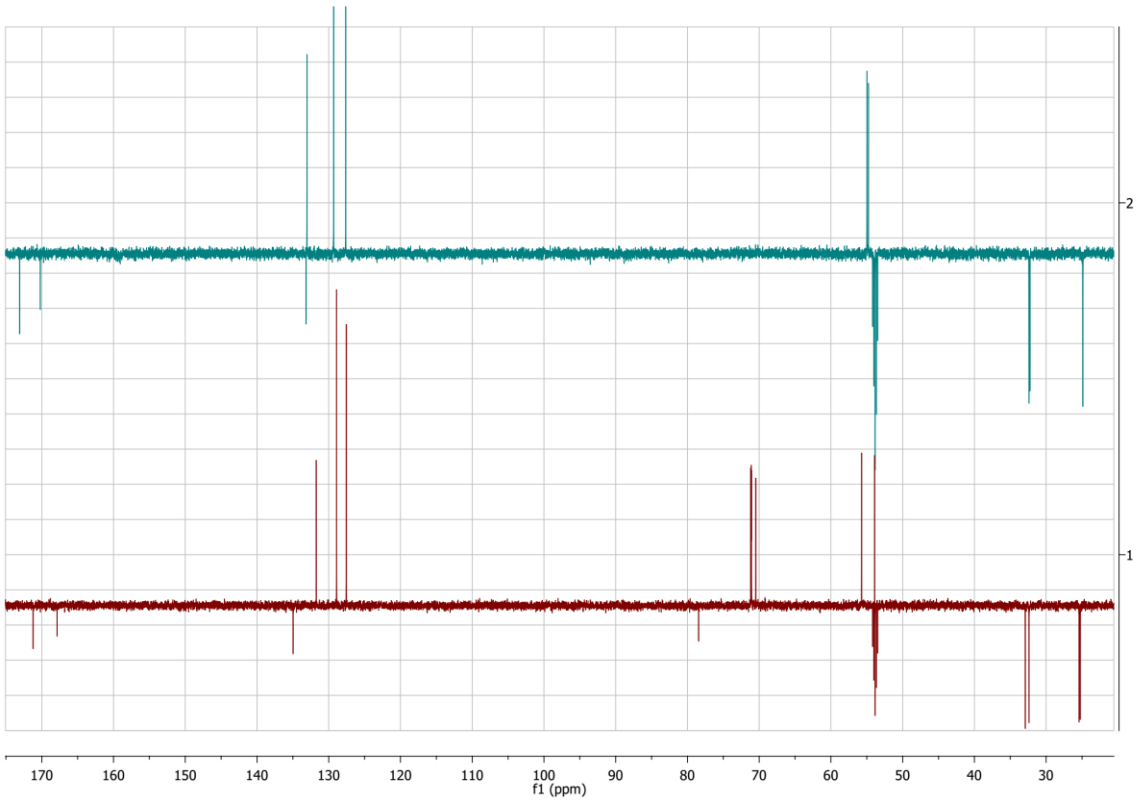
Bottom spectra is pure 2b in DCM (c= 5.60 mM), above spectra are with 2, 4 and 8 equivalents of TFA respectively.

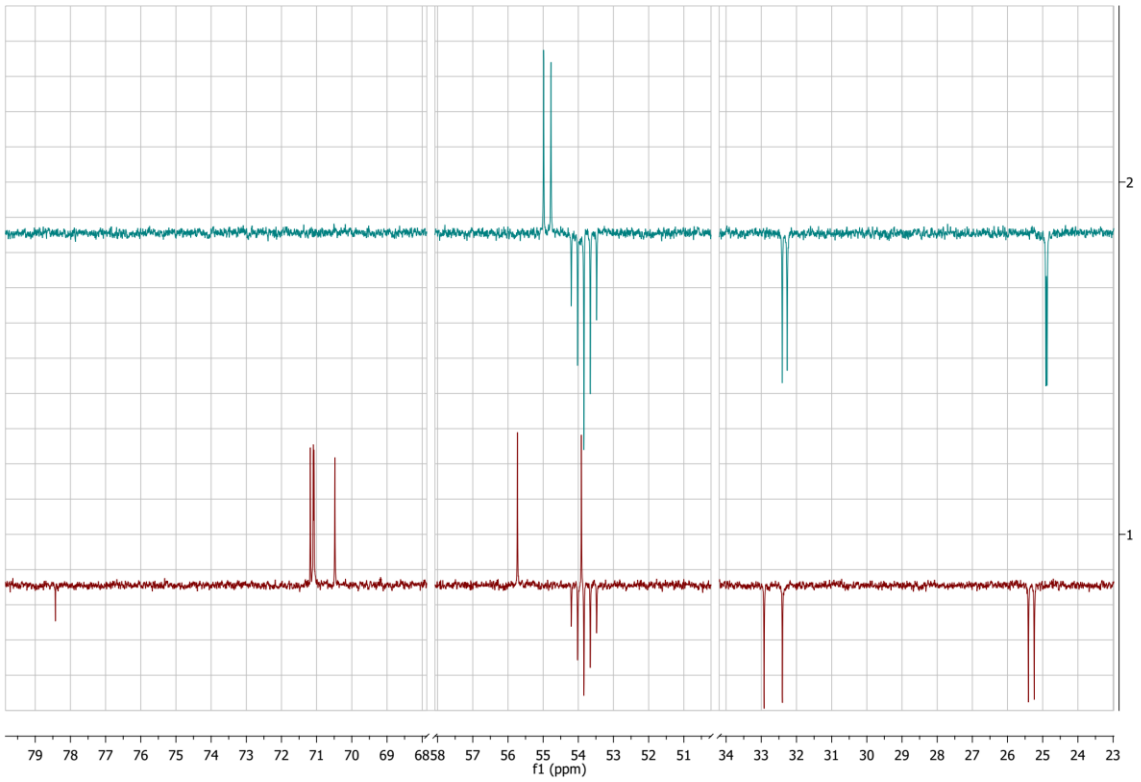
7.2 2b + excess TFA

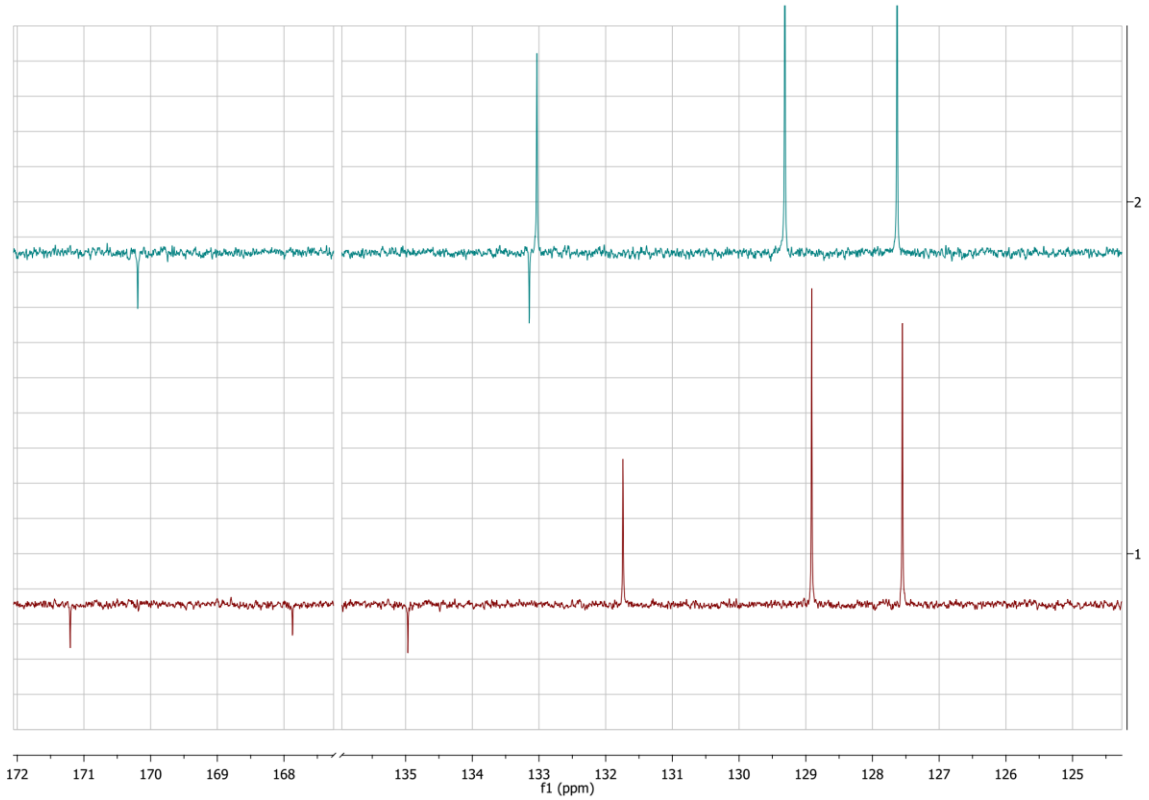


Bottom spectra is **2b** (c = 4.33 mM) in DCM, upper spectra is the same sample with 5 µ concentrated TFA.

8 ^{13}C NMR 2b + TFA







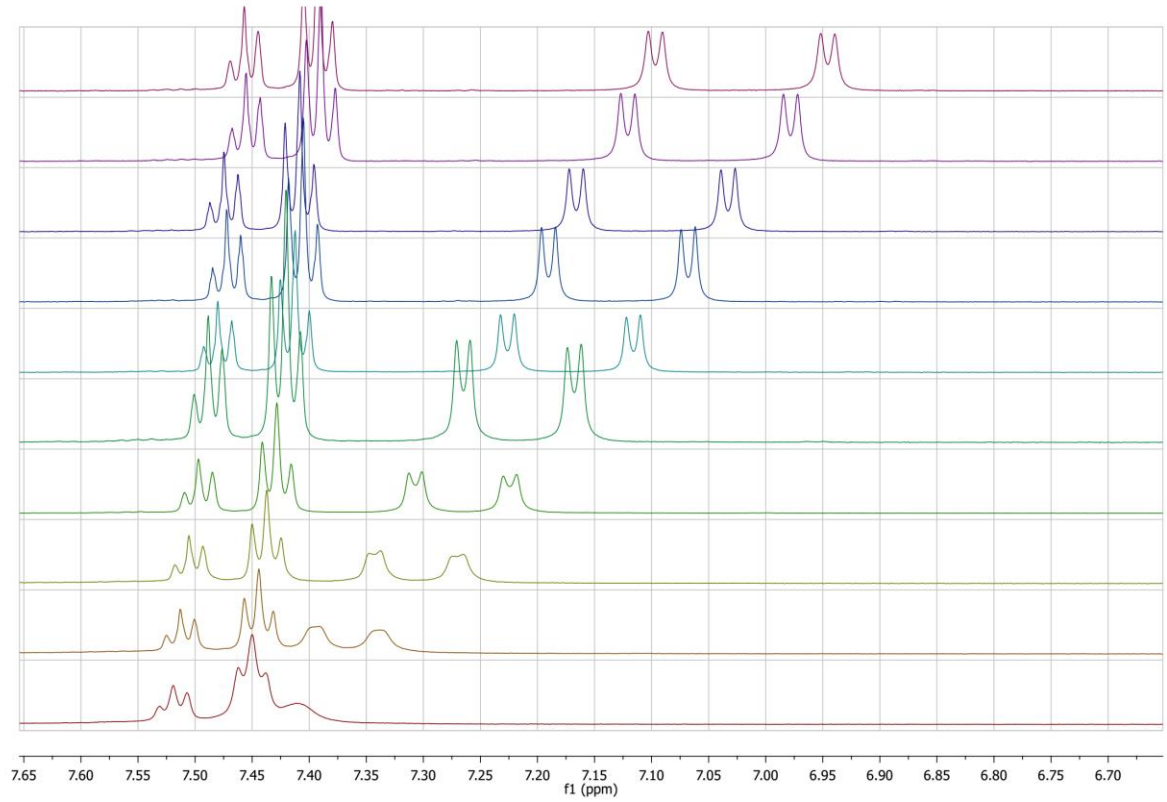
Lower spectra is **2b**, c(2b)= 29.4 mM, upper spectra is the same sample with 5 µL of concentrated TFA, c(2b)=29.1 mM.

9 Temperature ^{1}H NMR in Dichloroethane

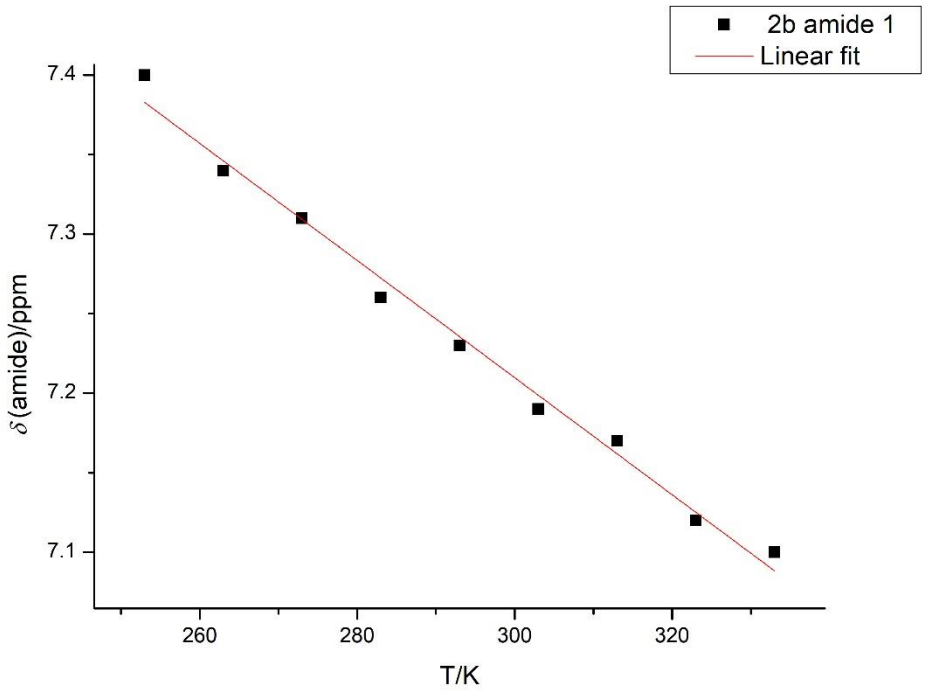
Data fitting was done by Origin 8.5 software.

9.1 2b

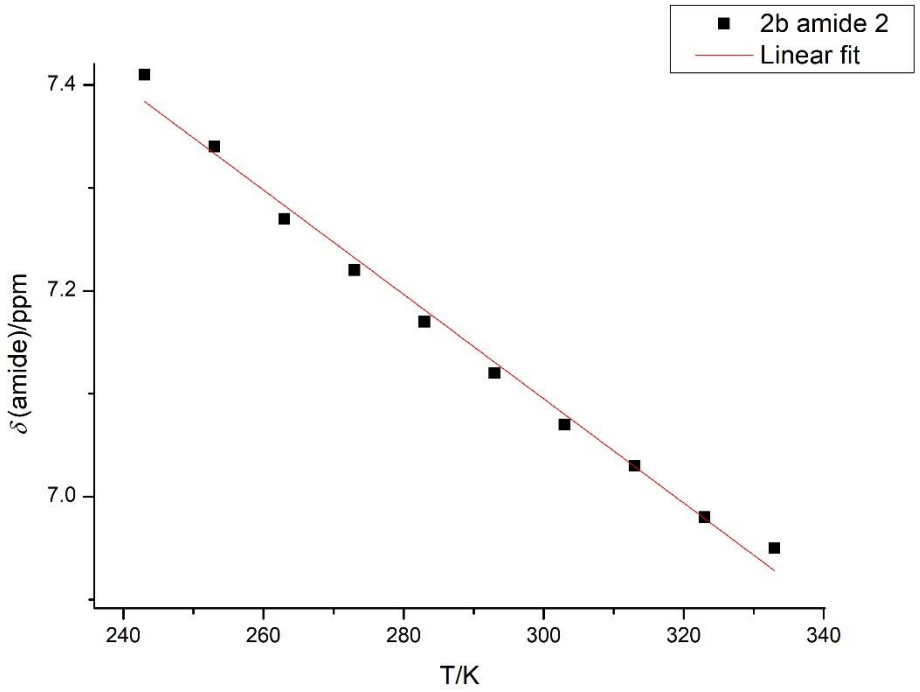
c= 8.71 m



Bottom spectra is at 243 K, spectra were recorded in 10 K intervals (bottom 243 K, top 333 K).



Intercept	Slope	R^2
8.31477	-0.00368	0.98859

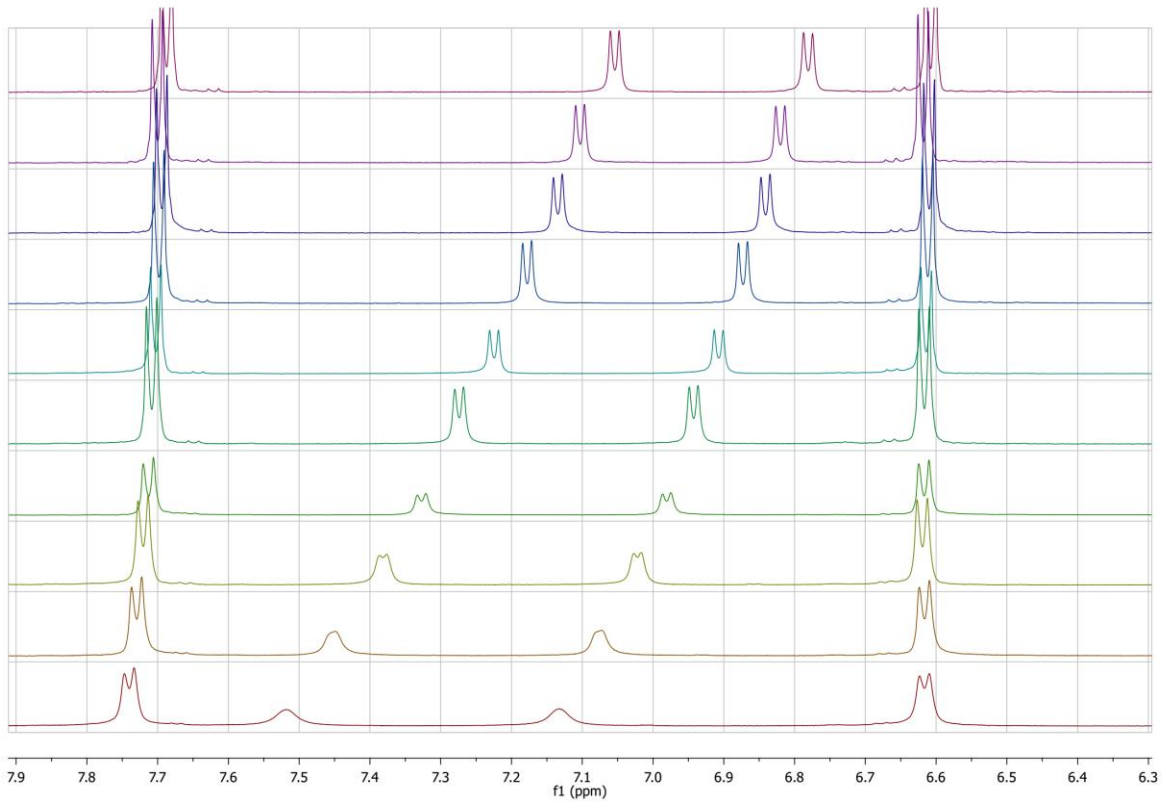


Intercept	Slope	R^2

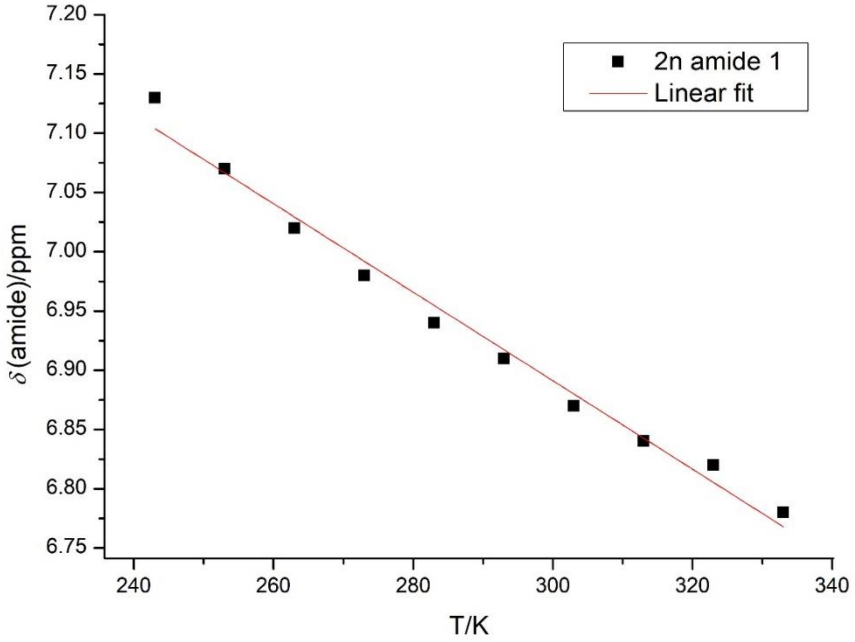
8.6152	-0.00507	0.99024

9.2 2n

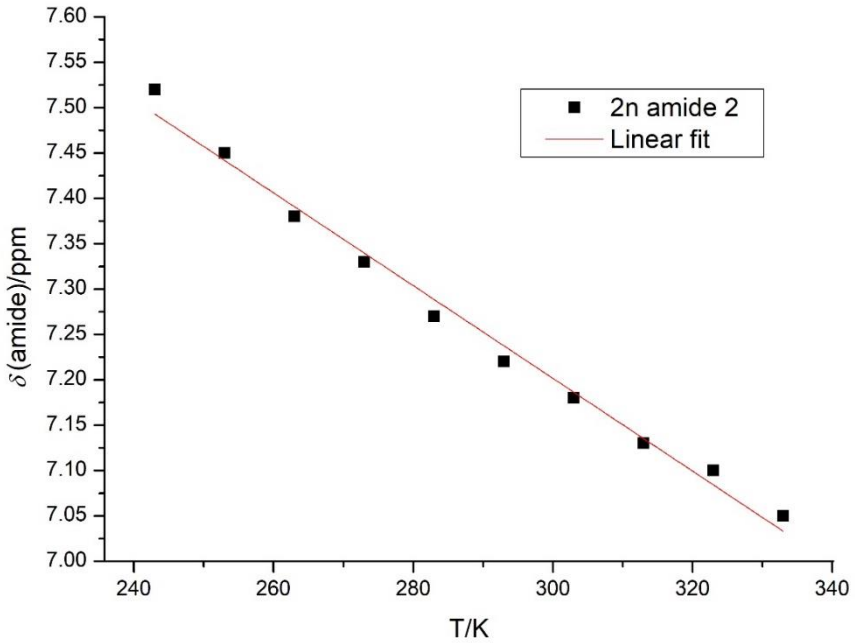
c = 8.64 mM



Bottom spectra is at 243 K, spectra were recorded in 10 K intervals (bottom 243 K, top 333 K).



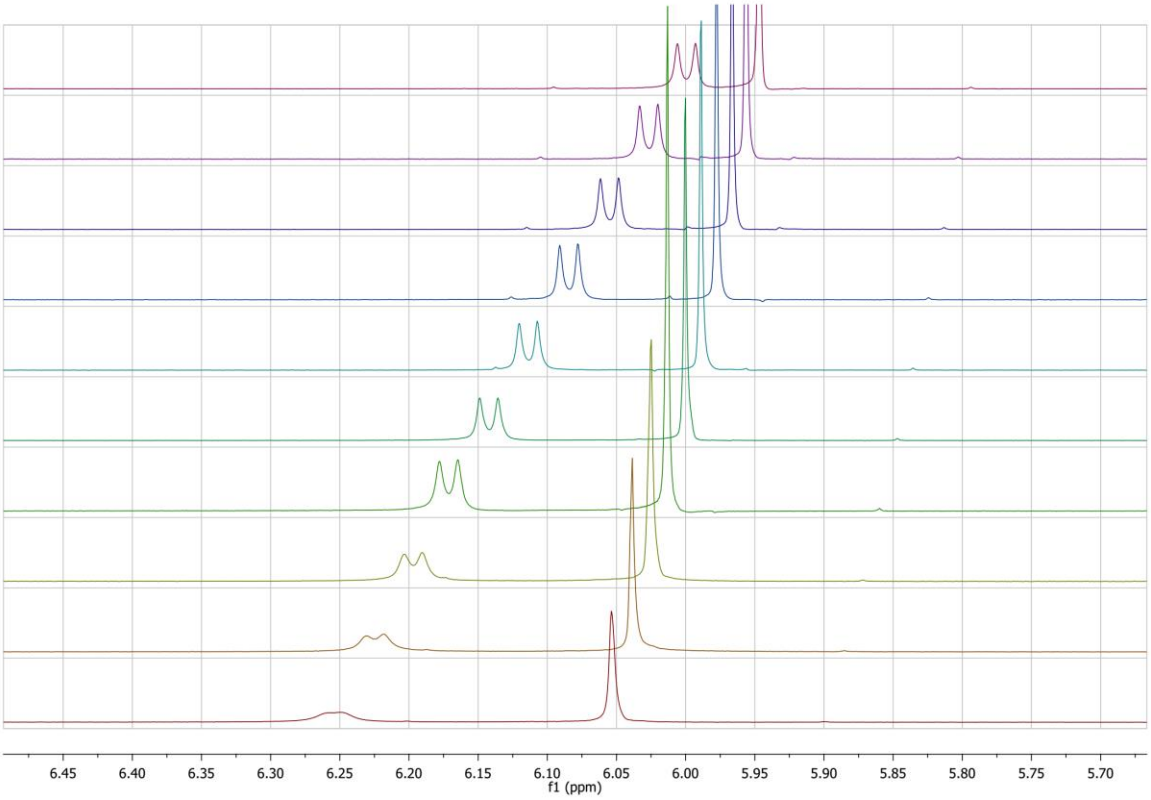
Intercept	Slope	R^2
8.0112	-0.00373	0.98405



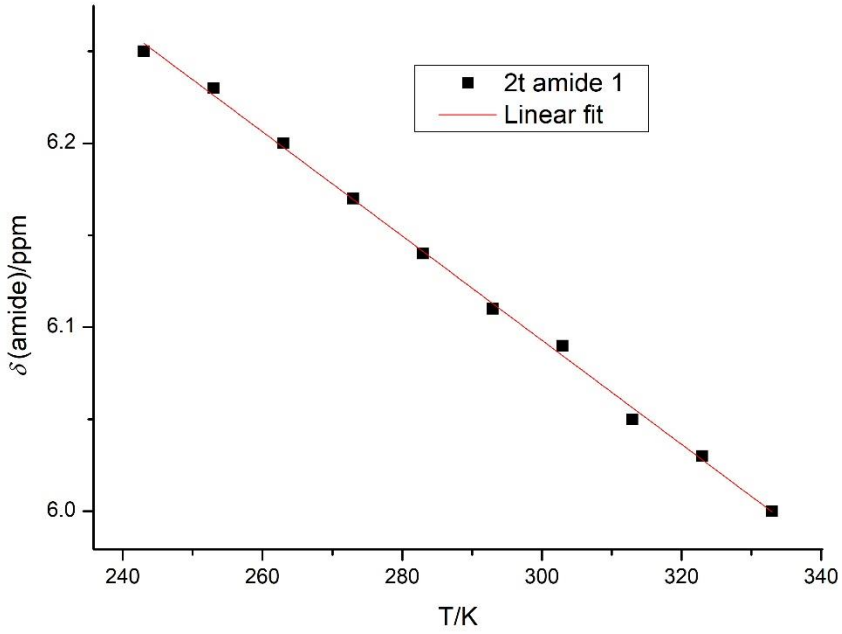
Intercept	Slope	R^2
8.73442	-0.00511	0.98831

9.3 2t

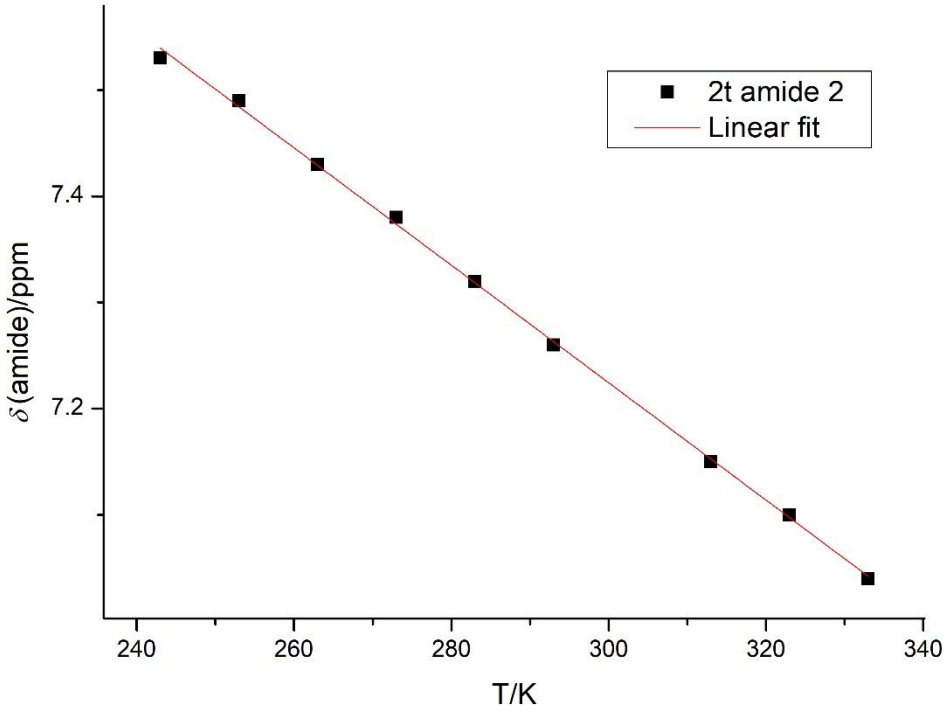
c = 7.9 mM



Bottom spectra is at 243 K, spectra were recorded in 10 K intervals (bottom 243 K, top 333 K).



Intercept	Slope	R^2
6.94213	-0.00283	0.99792



Intercept	Slope	R^2
8.88199	-0.00553	0.99909

10 Dosy NMR

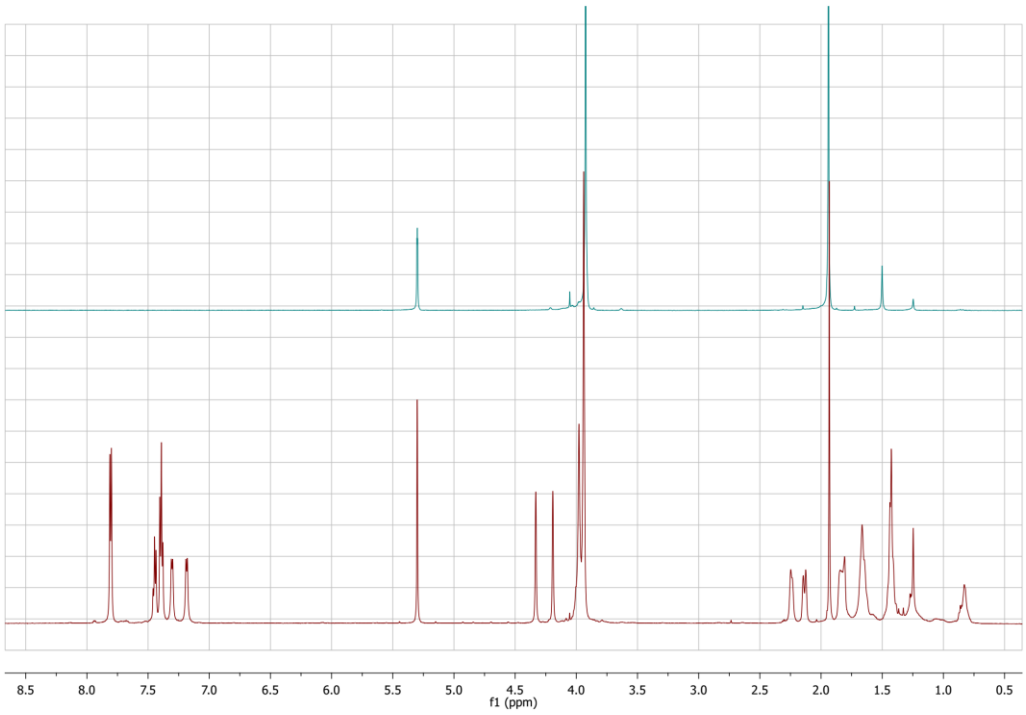
Compound	Concentration [mM]	Solvent	D [x10^{-10} m^{2}s^{-1}]	Radius [Å]	Volume [Å^3]
2b	8.45	DCM	9.27-9.49	5.57-5.70	23.33-23.87
2b	1.42	DCM	8.59-8.75	6.04-6.16	25.30-25.80
2b+8 eq. TFA	7.78	DCM	8.24-8.89	5.95-6.42	24.92-26.89
2b	7.78	MeOH	6.20-6.33	6.31-6.48	26.43-27.14
2b	1.66	MeOH	5.97-6.01	6.68-6.72	27.98-28.15
1b	10.63	DCM	11.5-11.8	4.47-4.59	18.72-19.22
1b	9.7	MeOH	8.06-8.34	4.81-4.98	20.15-20.86
2t	8.29	DCM	7.34-7.71	6.85-6.92	28.69-28.99
2t	7.87	MeOH	5.29-5.46	7.35-7.59	30.79-31.79
1t	8.26	DCM	9.52-10.1	5.23-5.55	21.91-23.25
1t	8.09	MeOH	6.91-6.97	5.76-5.81	24.13-24.34

The hydrodynamic radius was calculated from equation $D=(k\mathrm{B}T)/\zeta$, where $\zeta=6\pi\eta r$, kB is the Boltzmann constant, η the solvent viscosity (1 cP=10−3 kg m−1 s−1=10−3 Pa s) and r the molecule's radius . η(DCM) = 0.413 mPa s, η(MeOH) = 0.5435 mPa s. Since this equation is valid for the size of colloid particles in solvent (large size difference) the calculated radius **r** should be taken only qualitatively. The values of D shown are the maximal and minimal measured values from multiple experiments, the hydrodynamic radius was calculated from these values accordingly.

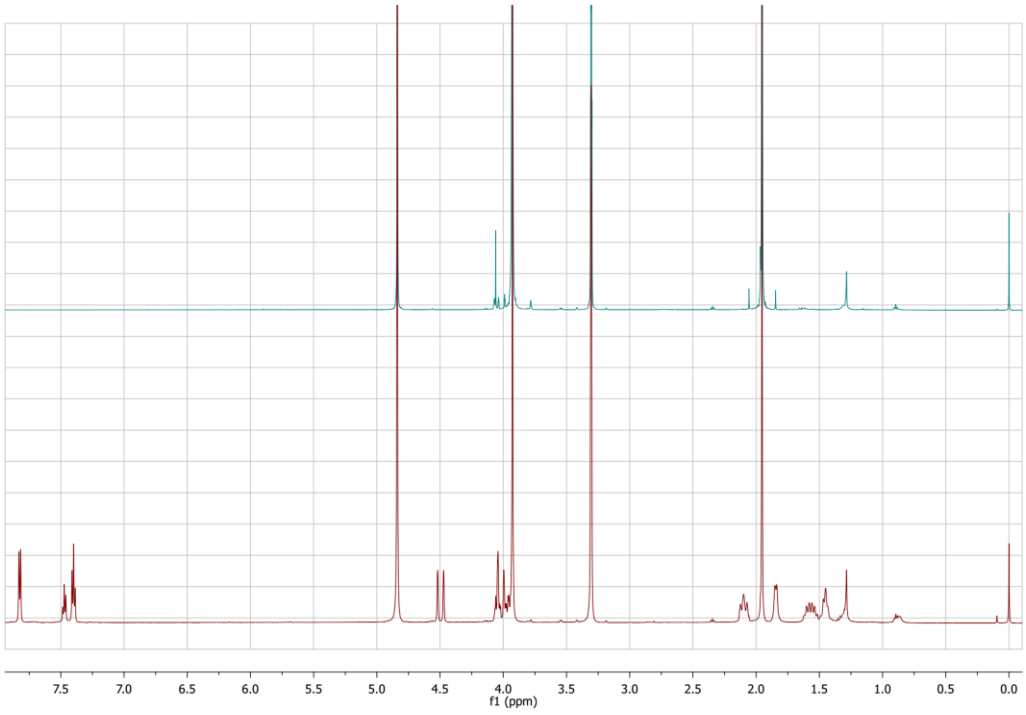
11 Nmr mass quantification experiment

In order to asses if proton NMR detects all of the dissolved compound **2b** or just an unaggregated fraction we have recorded spectra containing a mixture of **2b** and 1,1'dimethylferrocene. 1,1'dimethylferrocene was chosen as a mass standard as it contains no functional groups that could interfere with hydrogen bonding and has a well resolved methyl peak at 1.94 ppm. For calculations the isolated ferrocene peak of **2b** at 4.33 ppm (corresponding to 2 protons) was used. Multiple measurements with different mass ratios of **2b** and 1,1'dimethylferrocene were performed.

Mass percentages were calculated from NMR spectra using the equation $W_x = \frac{1}{1+\frac{I_y}{I_x}\cdot\frac{N_x}{N_y}\cdot\frac{M_y}{M_x}}$, where I is the intensity (integral) of the signal, N is the number of protons, and M is the molar mass.

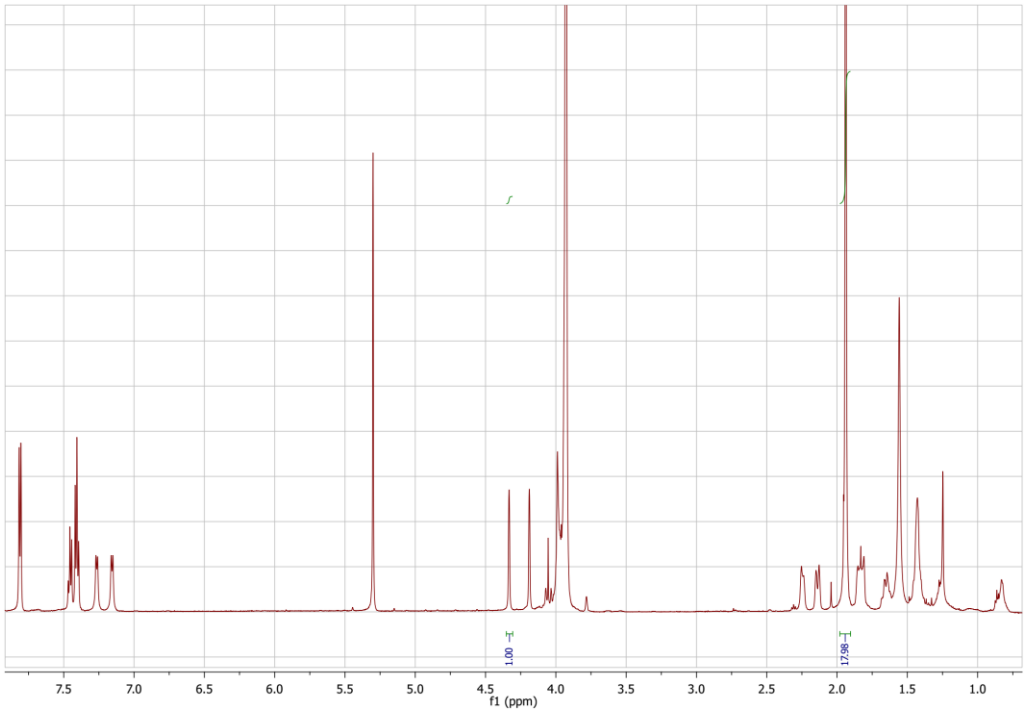


Proton NMR spectra of 1,1'dimethylferrocene (upper) and a mixture of **2b** and 1,1'dimethylferrocene (lower) in DCM.

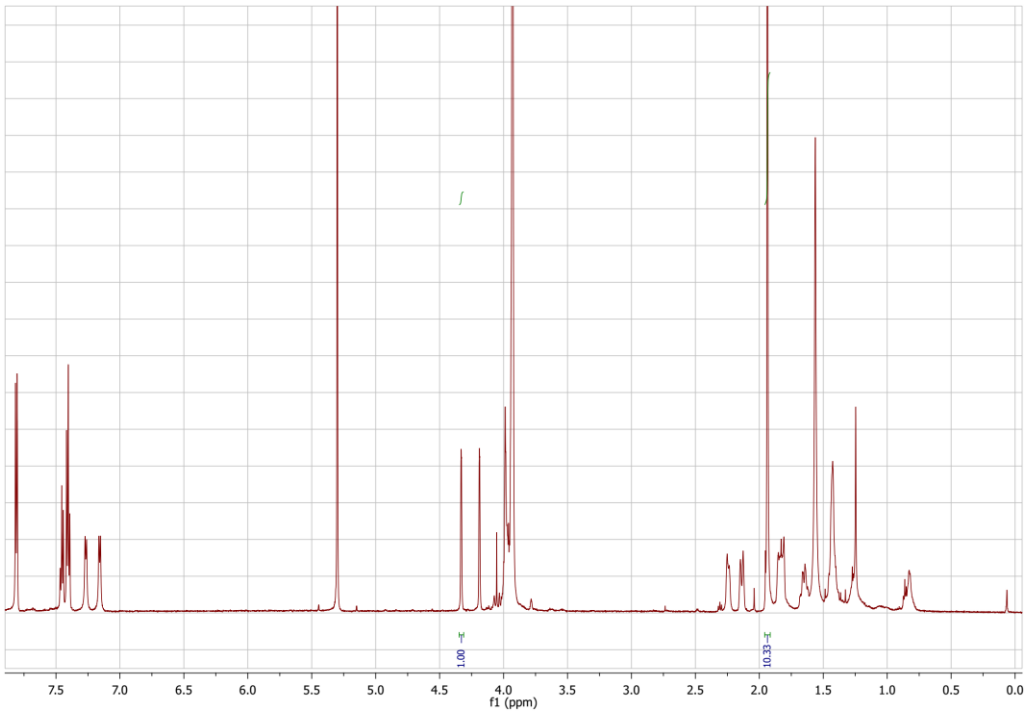


Proton NMR spectra of 1,1'dimethylferrocene (upper) and a mixture of **2b** and 1,1'dimethylferrocene (lower) in MeOD.

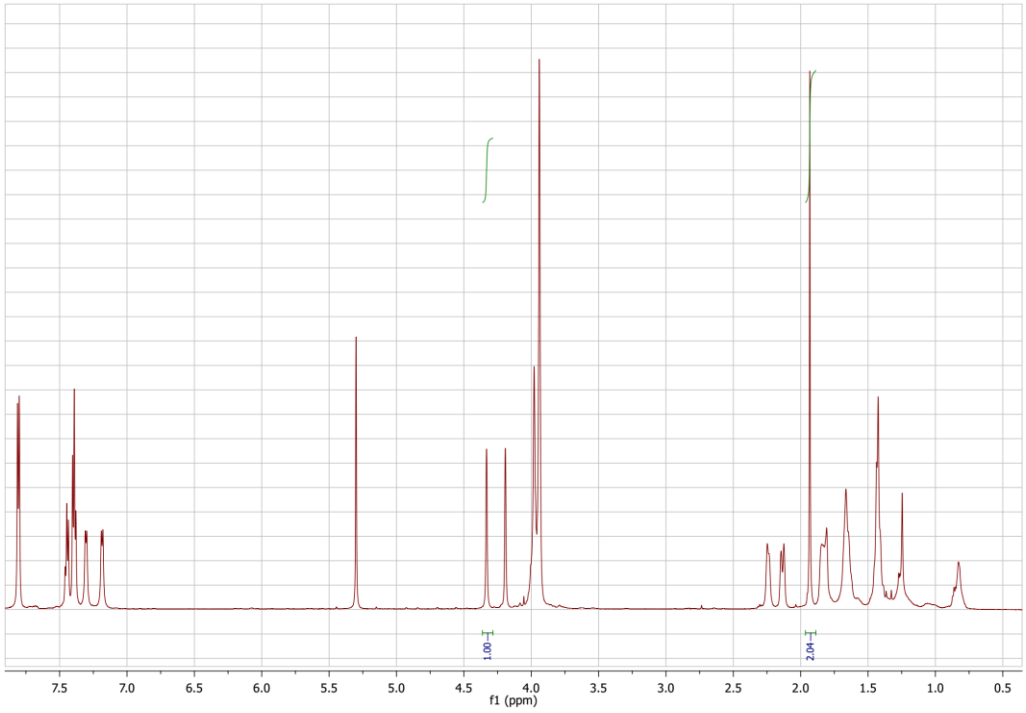
11.1 DCM measurements



m (1,1'dimethylferrocene) = 4.02 mg, m (**2b**) = 1.97 mg, w (**2b**) = 33 %, w (**2b,** from NMR) = 34 %.

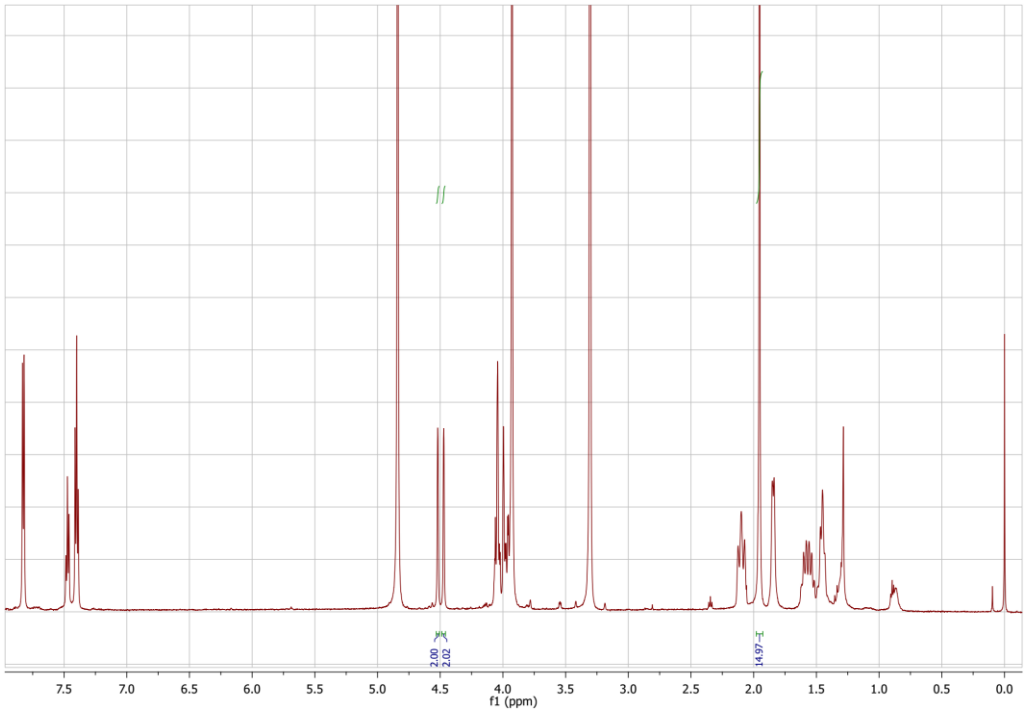


m (1,1'dimethylferrocene) = 1.96 mg, m (**2b**) = 1.90 mg, w (**2b**) = 49 %, w (**2b,** from NMR) = 48 %.

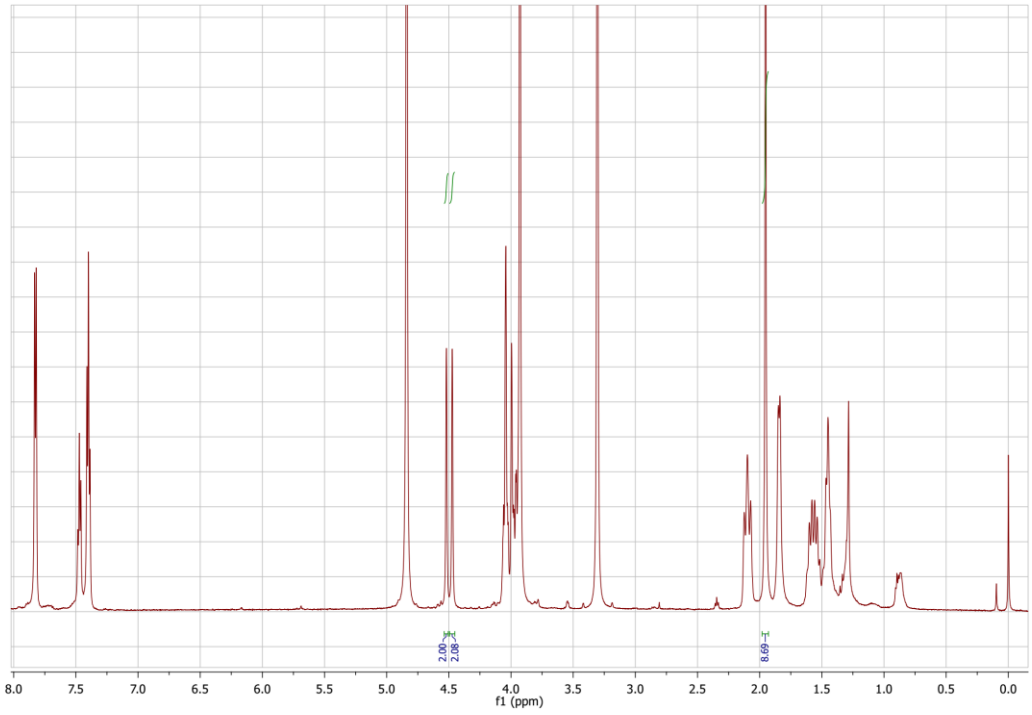


m (1,1'dimethylferrocene) = 1.03 mg, m (**2b**) = 5.33 mg, w (**2b**) = 84 %, w (**2b,** from NMR) = 83 %.

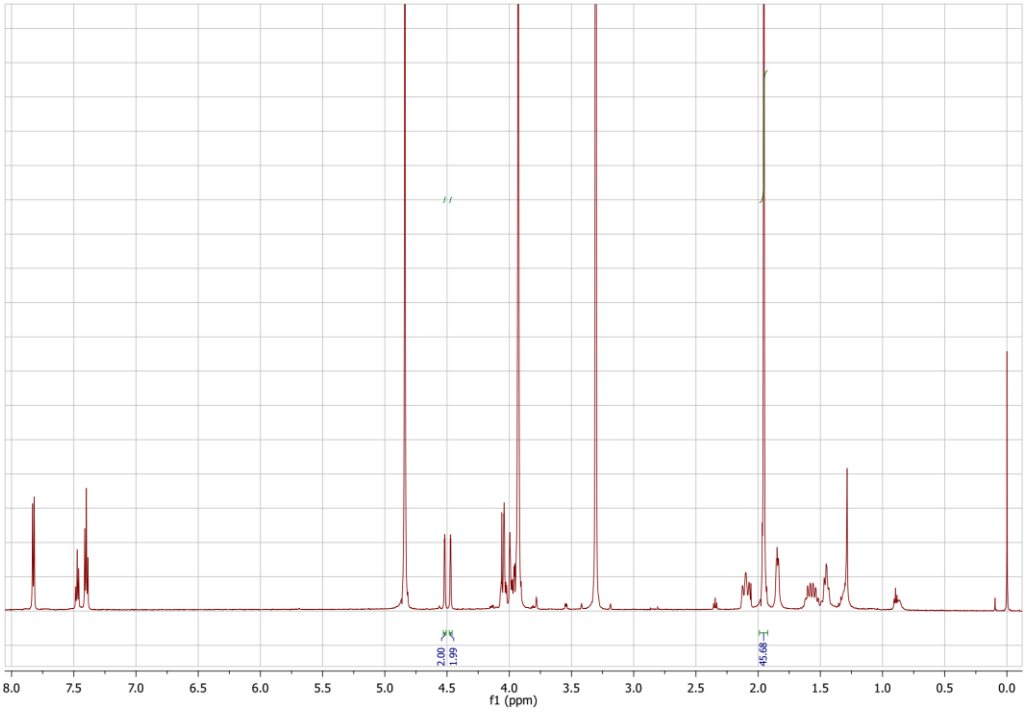
11.2 MeOH measurements



m (1,1'dimethylferrocene) = 1.23 mg, m (**2b**) = 1.66 mg, w (**2b**) = 57 %, w (**2b,** from NMR) = 56 %.



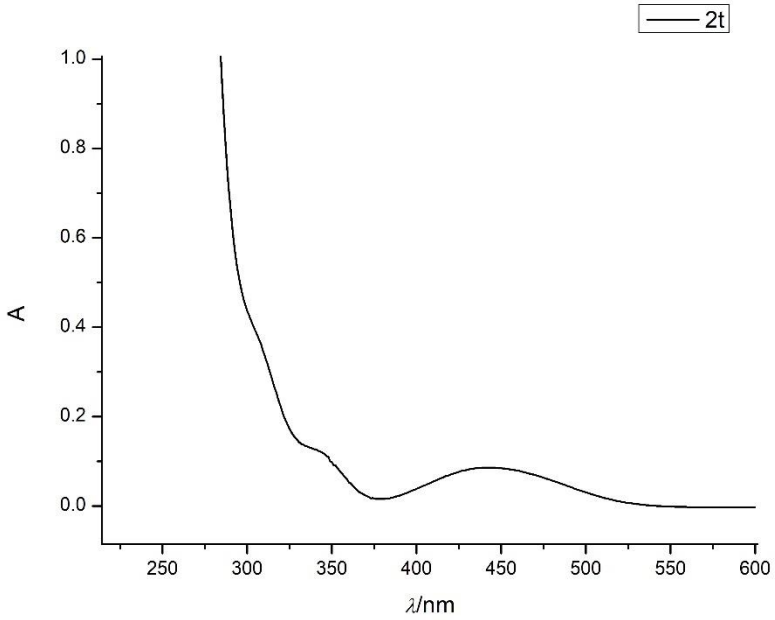
m (1,1'dimethylferrocene) = 1.26 mg, m (**2b**) = 3.18 mg, w (**2b**) = 72 %, w (**2b,** from NMR) = 69%.



m (1,1'dimethylferrocene) = 2.14 mg, m (**2b**) = 0.91 mg, w (**2b**) = 30 %, w (**2b,** from NMR) = 29 %.

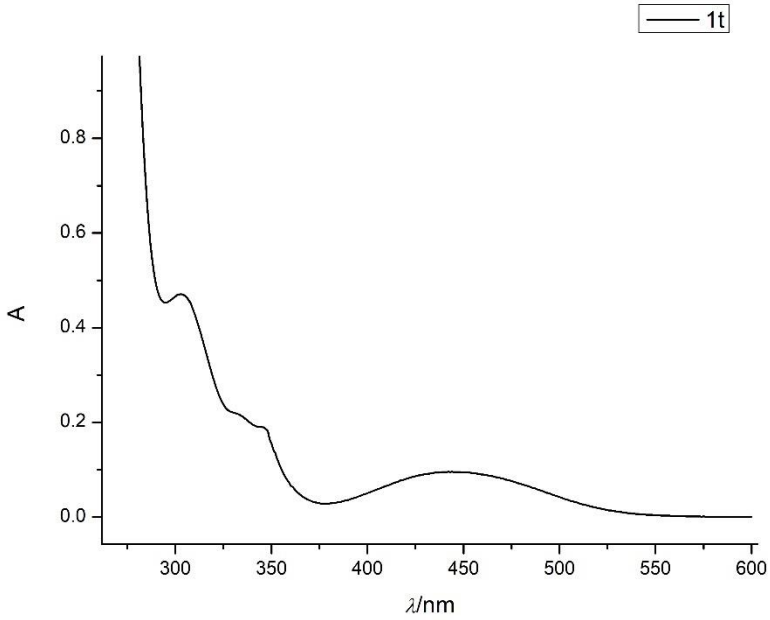
12 Uv/Vis spectra in dcm

12.1 2t



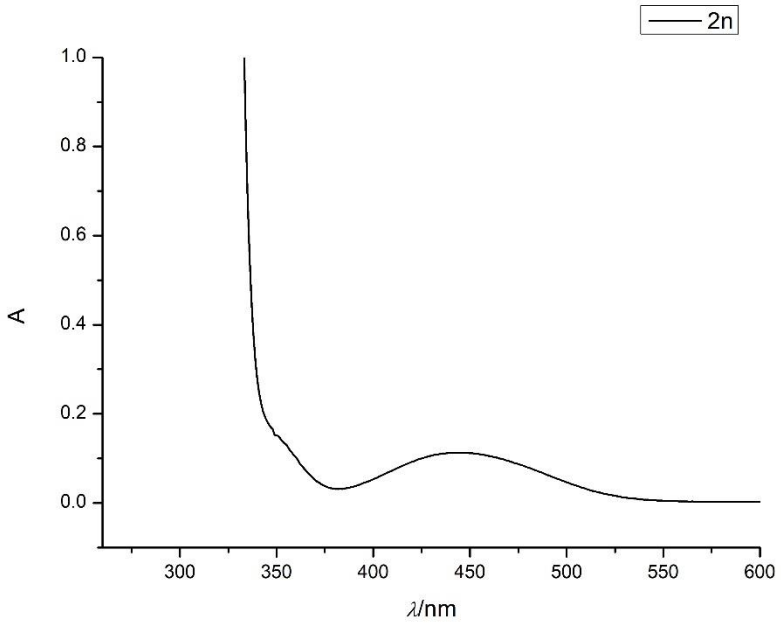
c= 4.051 mM

12.2 1t



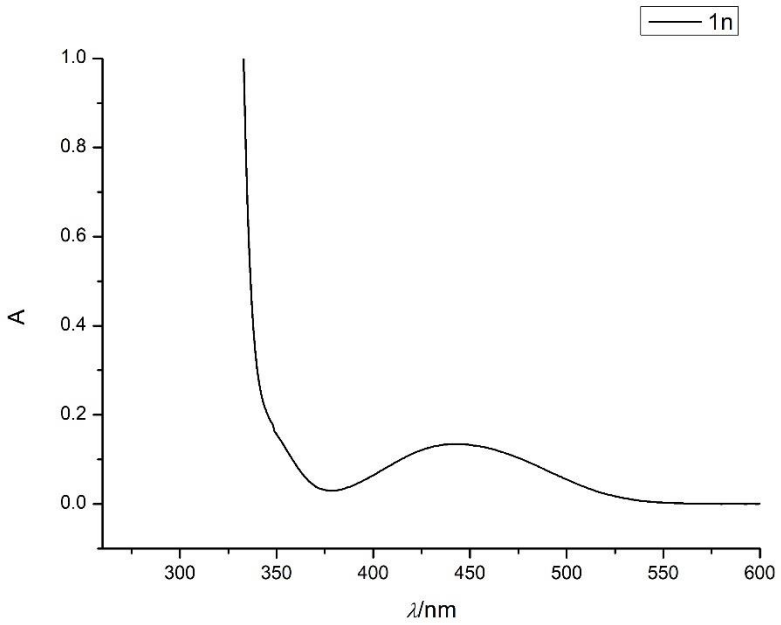
c= 4.241 mM

12.3 2n



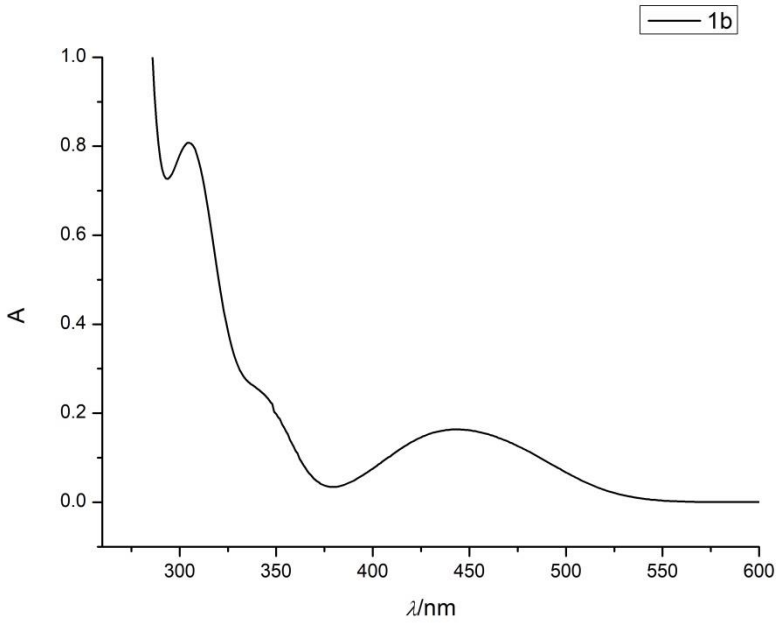
c = 5.26 mM

12.4 1n



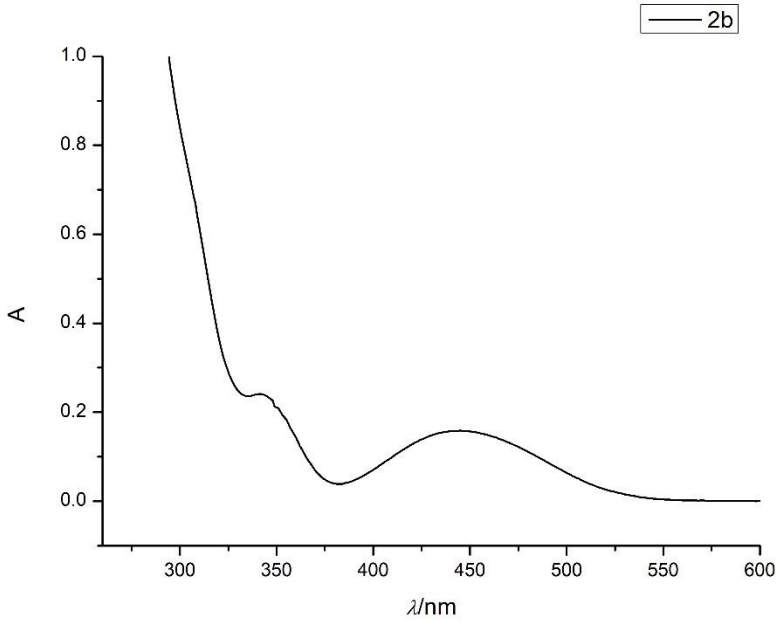
c = 7.22 mM

12.5 1b



c = 8.18 mM

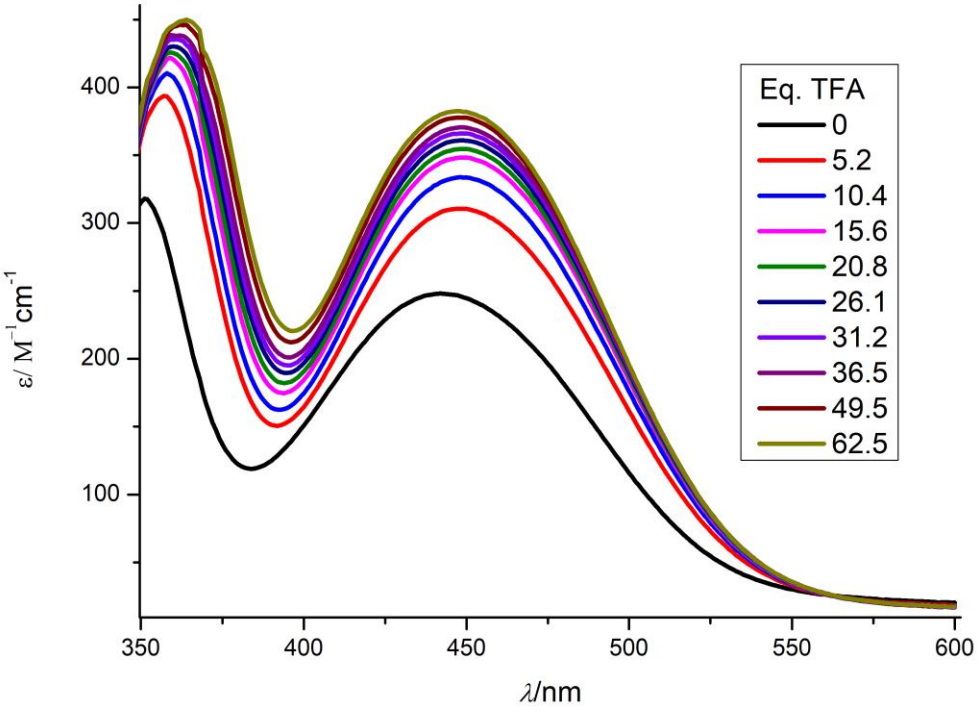
12.6 2b



c = 6.85 mM

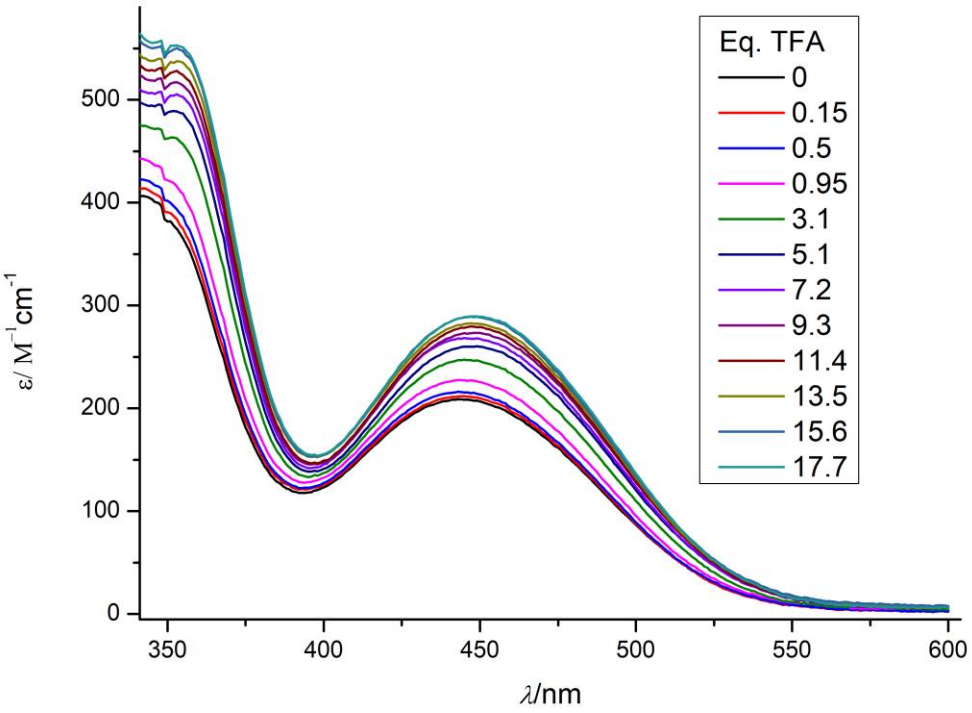
13 Uv-Vis spectra of 2b + TFA

13.1 UV spectra of 2b in DCM + TFA c =5 mM



c (2b) = 4.89-5.01 mM

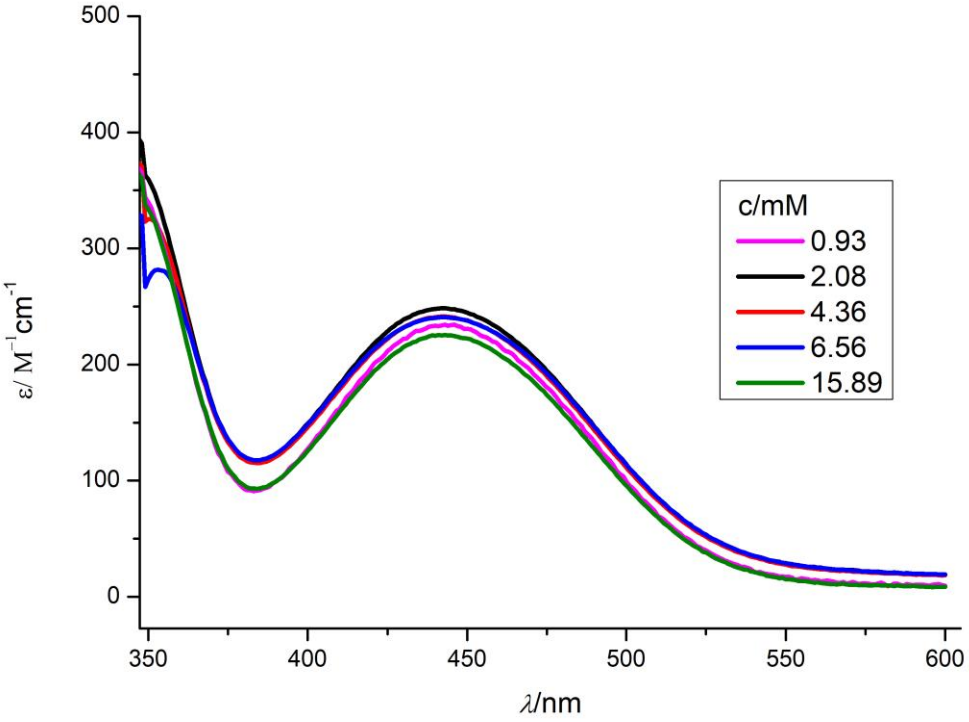
13.2 UV spectra of 2b in DCM + TFA c =0.5 mM



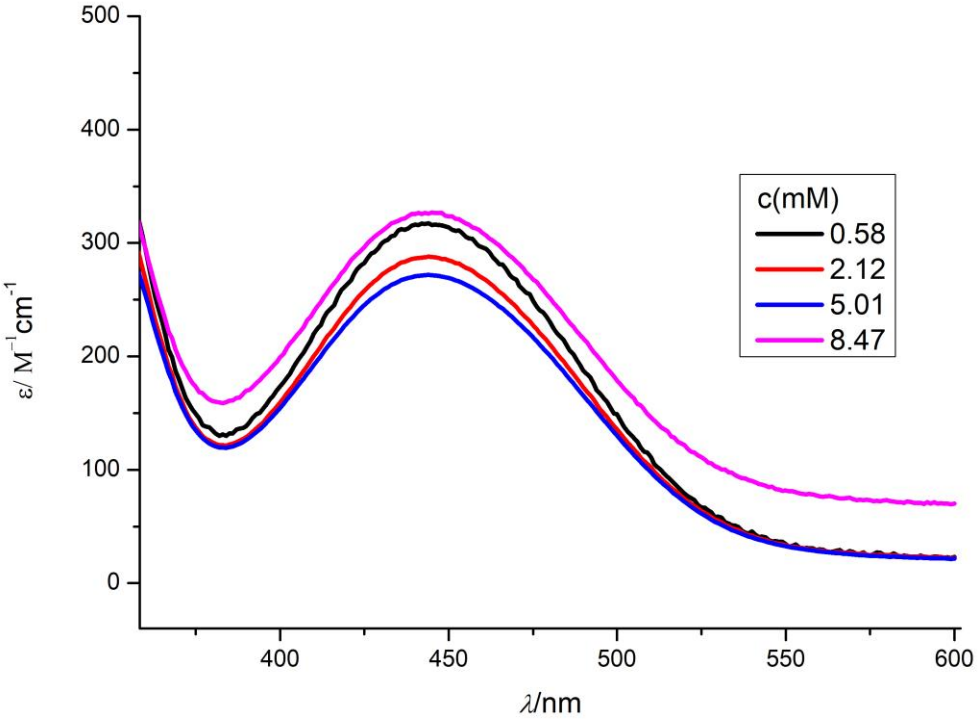
c = 0.53-0.61 mM

14 Concentration UV-Vis spectra

14.1 2b in DCM



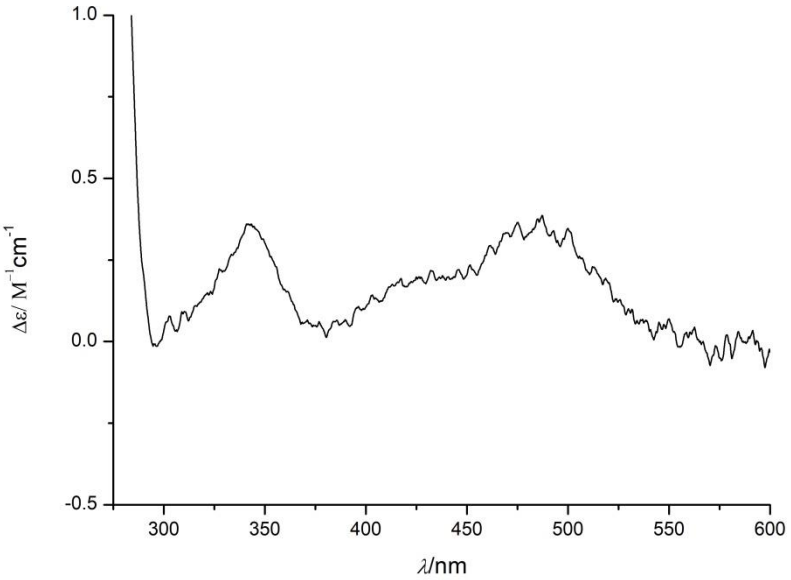
14.2 2b in MeOH



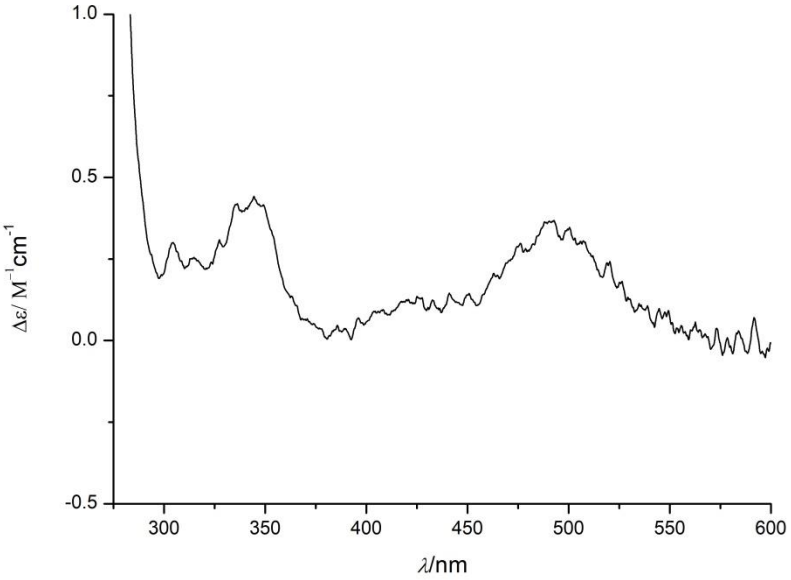
The elevated baseline at 8.47 mM is due to precipitation at this concentration.

15 Basic CD spectra in DCM

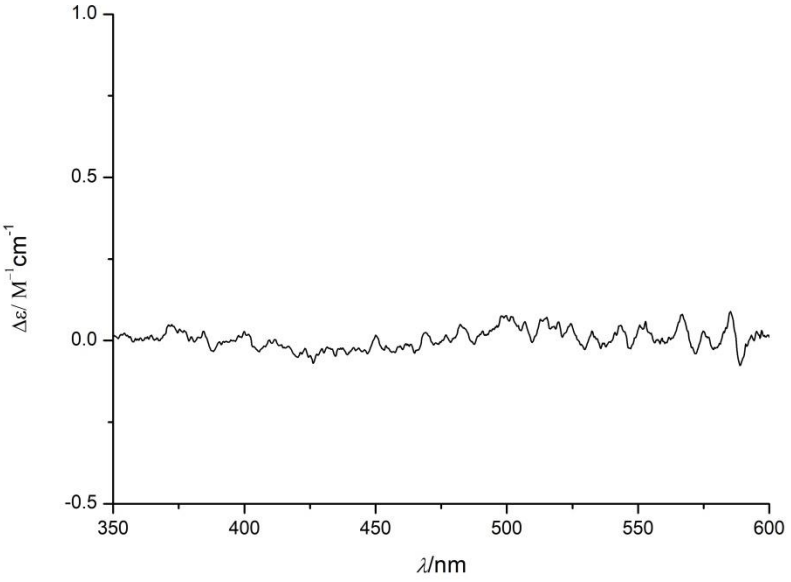
15.1 1t



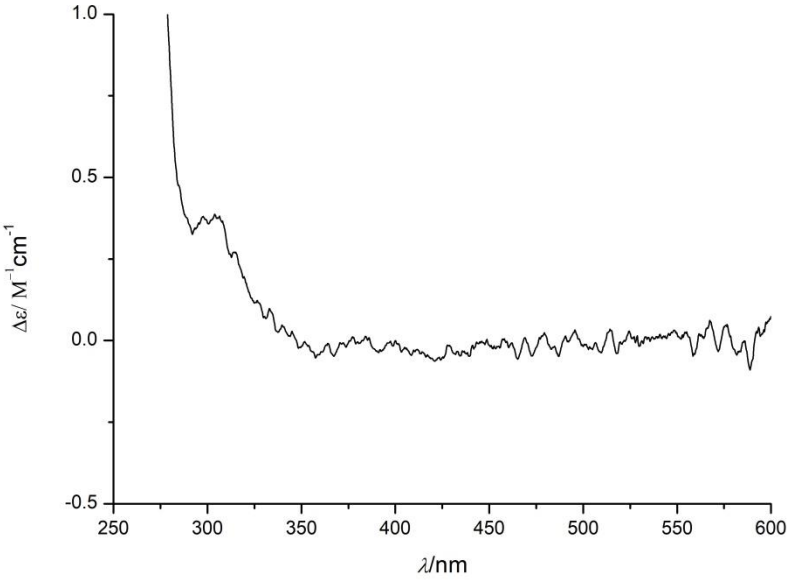
15.2 2t



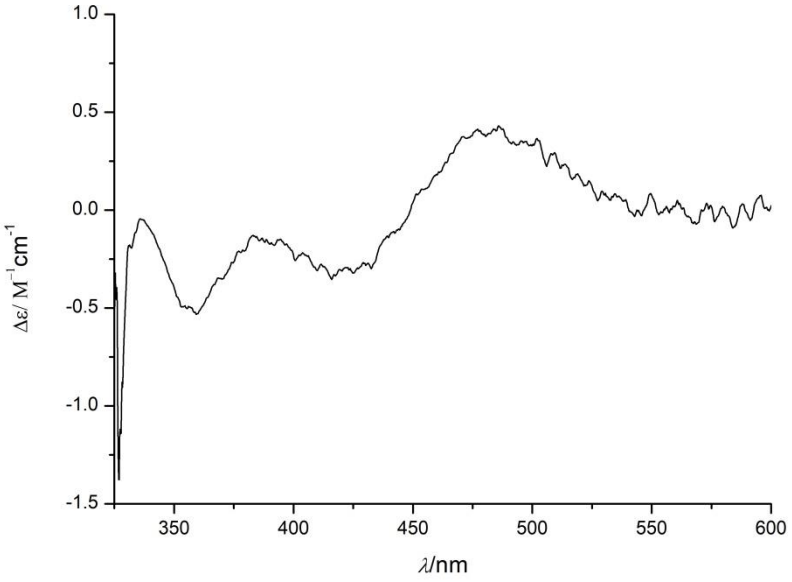
15.3 1n


1.0
0.5
0.0
-0.5
350
400
450
500
550
600
Δε/ M⁻¹cm⁻¹
λ/nm

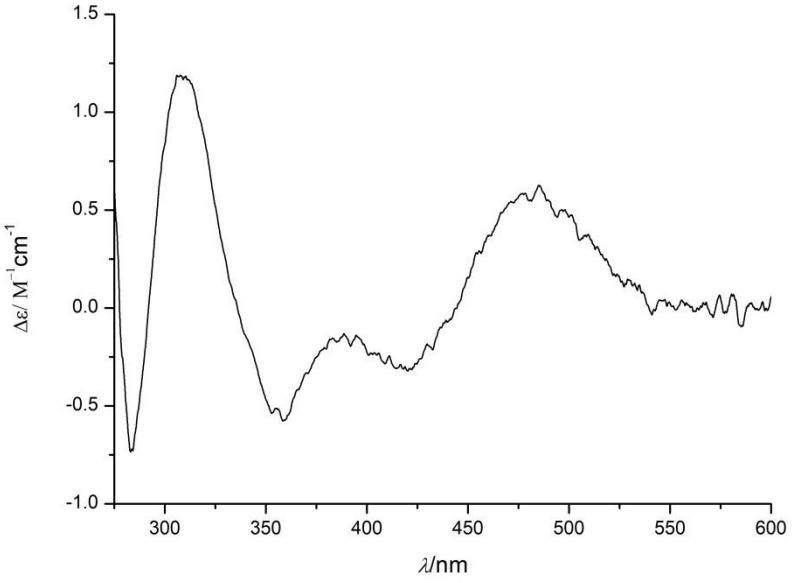
15.4 1b


1.0
0.5
0.0
-0.5
250
300
350
400
450
500
550
600
Δε/ M⁻¹cm⁻¹
λ/nm

15.5 2n

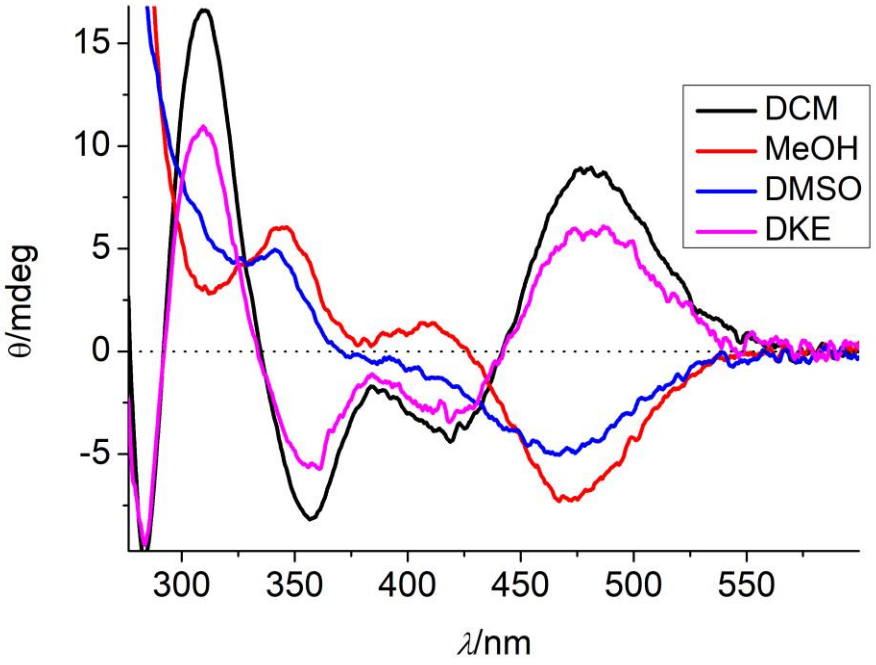

1.0
0.5
0.0
-0.5
-1.0
-1.5
350
400
450
500
550
600
Δε/ M⁻¹cm⁻¹
λ/nm

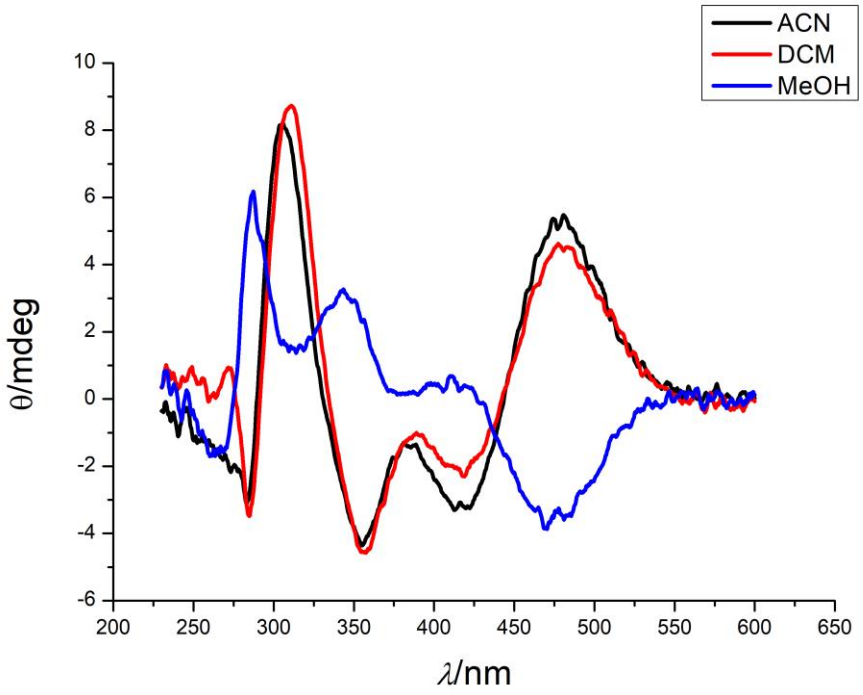
15.6 2b


1.5
1.0
0.5
0.0
-0.5
-1.0
300
350
400
450
500
550
600
Δε/ M⁻¹cm⁻¹
λ/nm

16 Variable solvent cd spectra

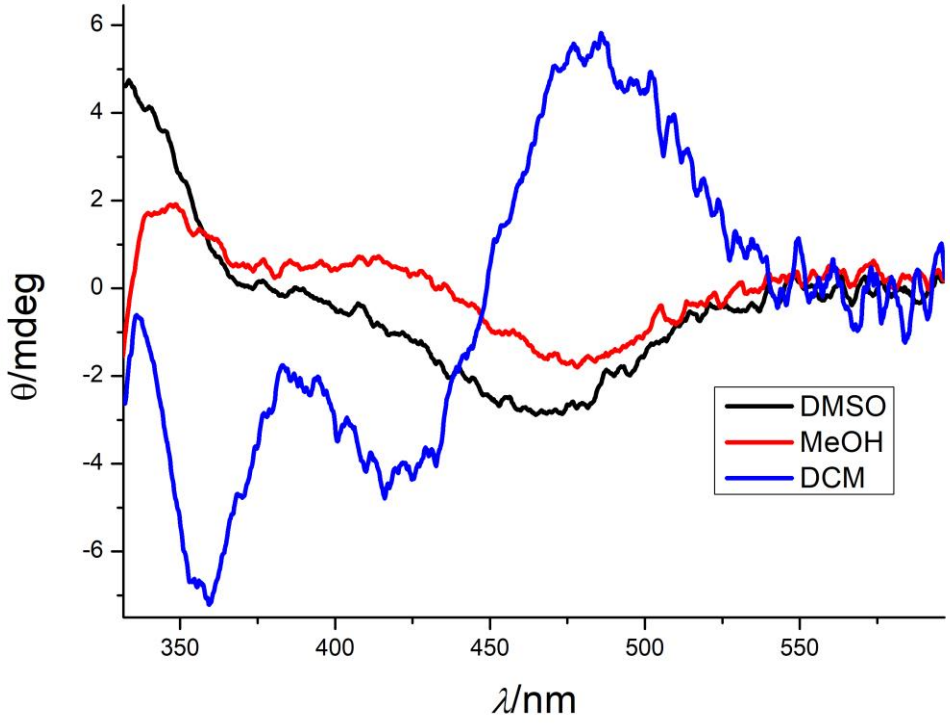
16.1 2b





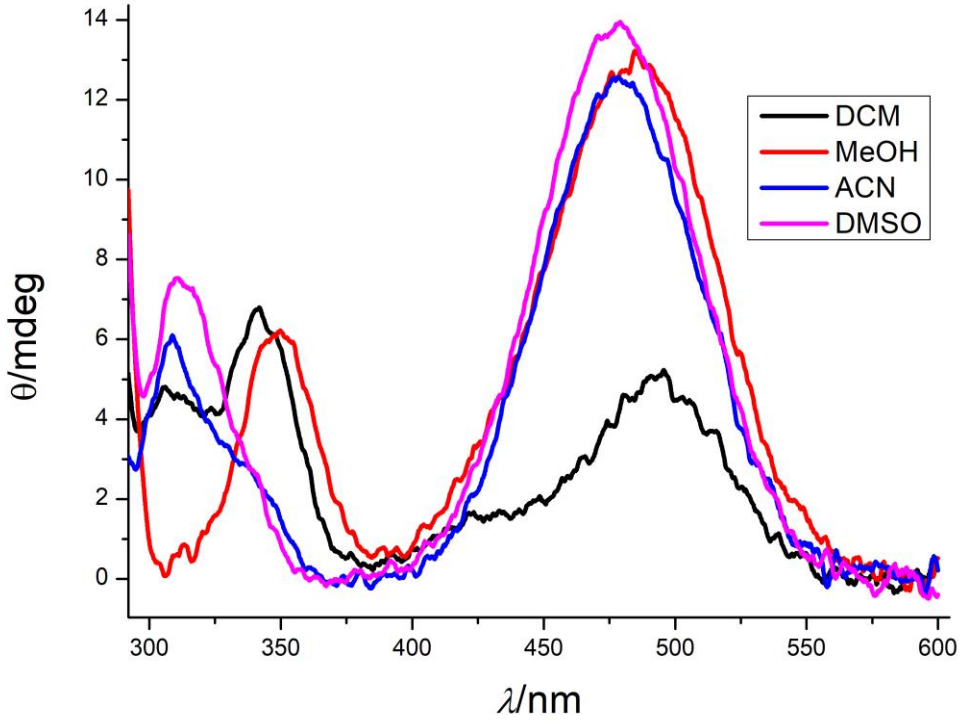
c (DCM) = 0.563 mM, c (MeOH) = 0.408, c (ACN) = 0.405 mM.

16.2 2n



c (DCM) = 4.10 mM, c (MeOH) = 0.96 mM, c (DMSO) = 2.54 mM.

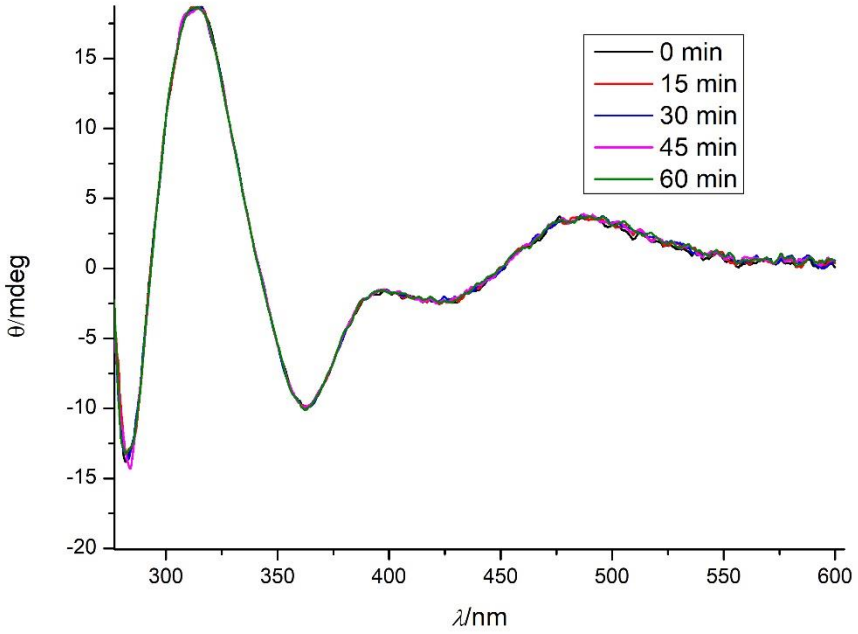
16.3 2t



c (DCM) = 4.01 mM, c (MeOH) = 4.11 mM, c (DMSO) = 3.97 mM, c (ACN) = 3.89 mM.

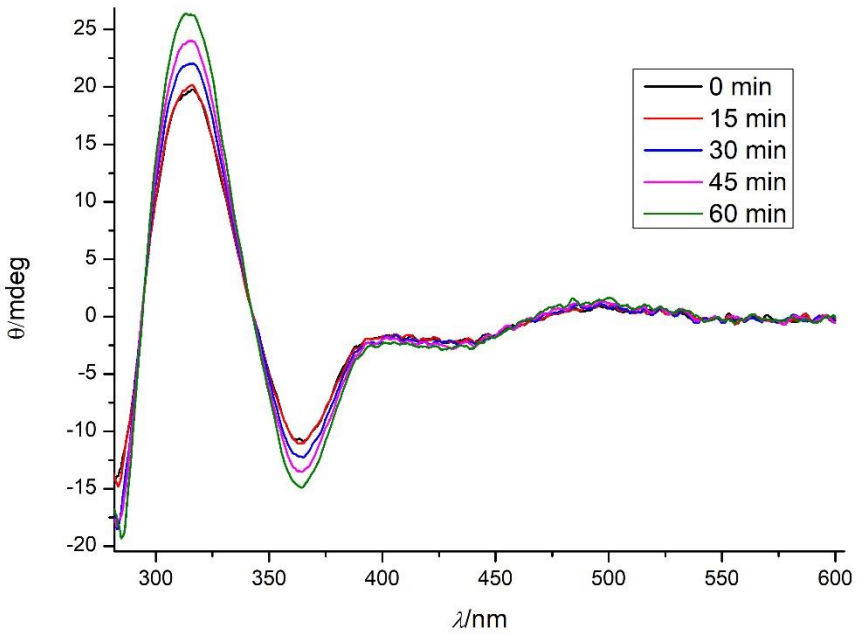
17 Cd spectra of 2b + TFA

17.1 CD spectra of 2b in DCM + ≈1 equivalent TFA during 1 hour



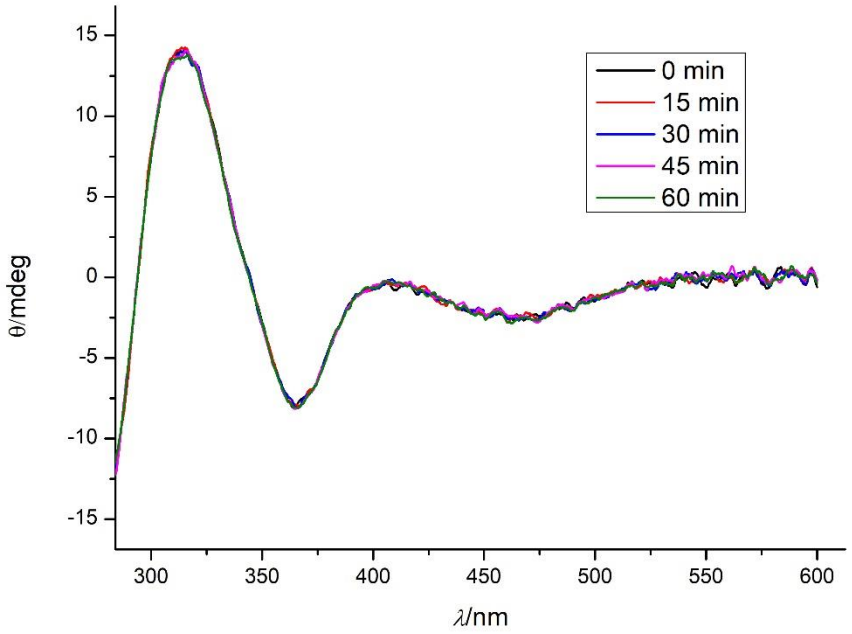
c = 4.78 mM

17.2 CD spectra of 2b in DCM + ≈2 equivalents of TFA during 1 hour



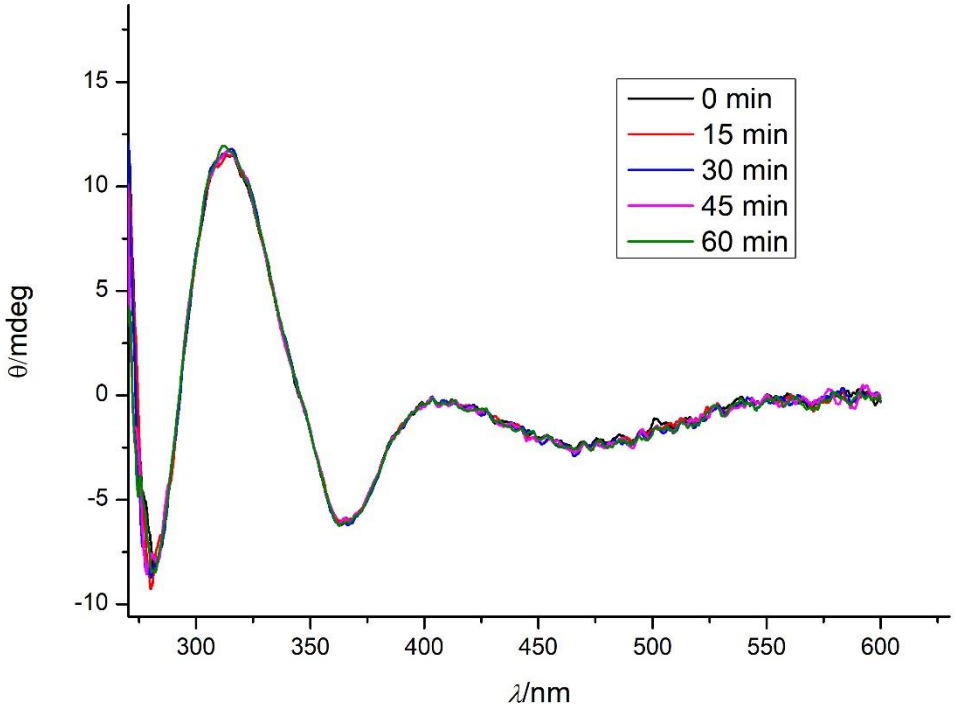
c = 5.44 mM

17.3 CD spectra of 2b in DCM + ≈3 equivalents of TFA during 1 hour



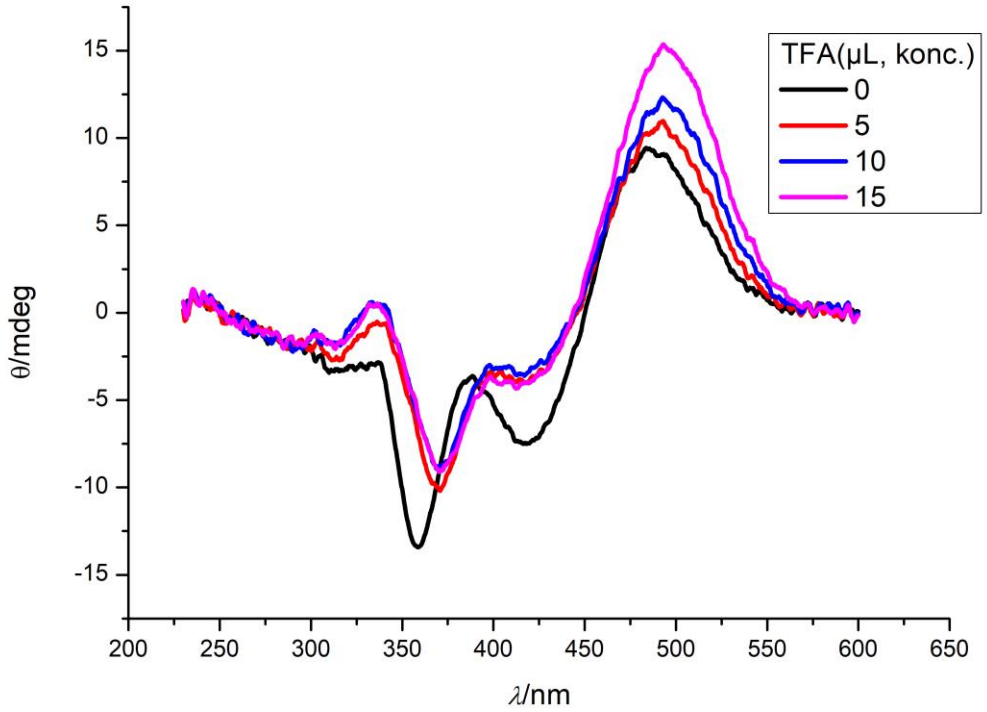
c = 4.61 mM

17.4 CD spectra of 2b in DCM + ≈4 equivalents of TFA during 1 hour



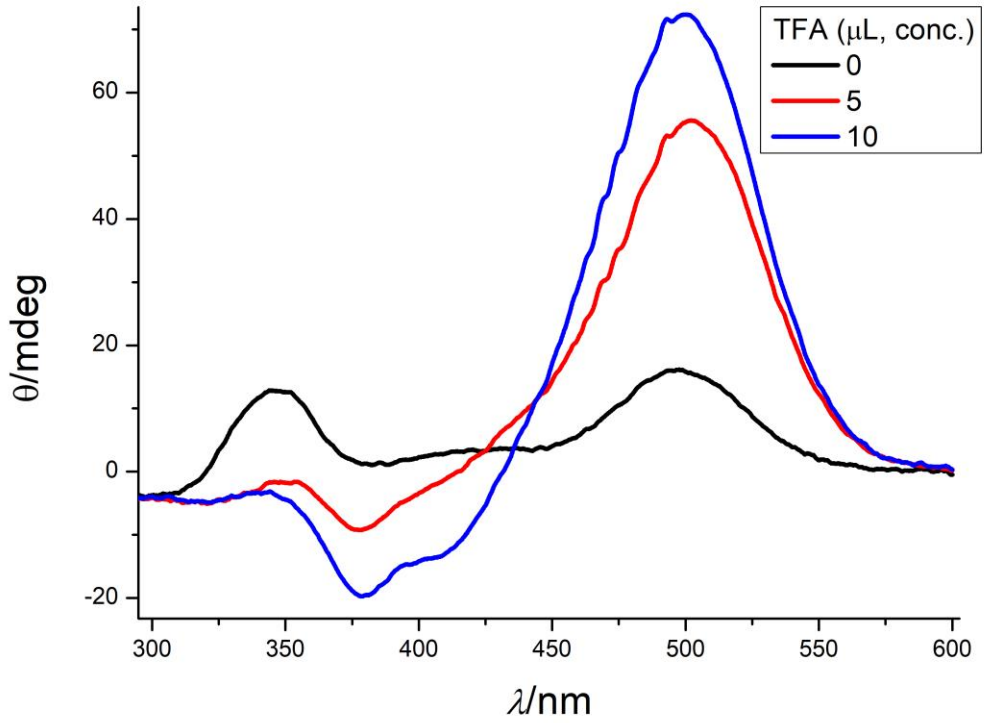
c = 3.39 mM

18 CD spectra of 2n+TFA



c=1.28-1.30 mM. Inversion is not observed When TFA is added to a DCM solution of **2n.**

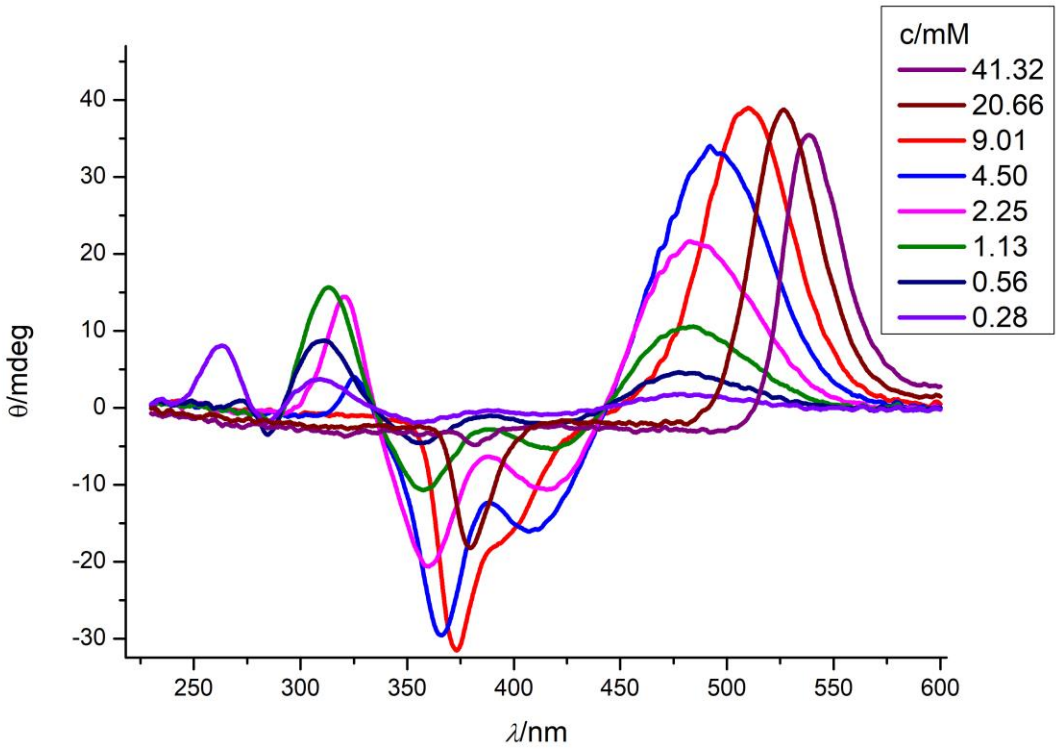
19 CD spectra of 2t + TFA



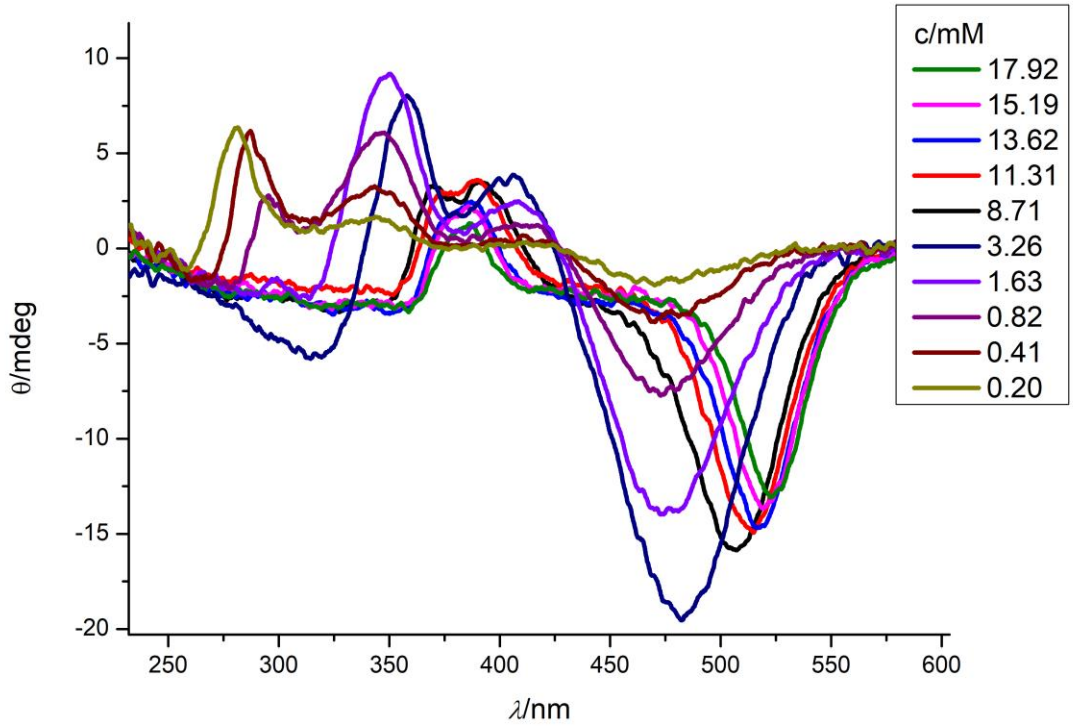
c(2t) = 2.27 mM-2.25 mM

20 Concentration CD spectra

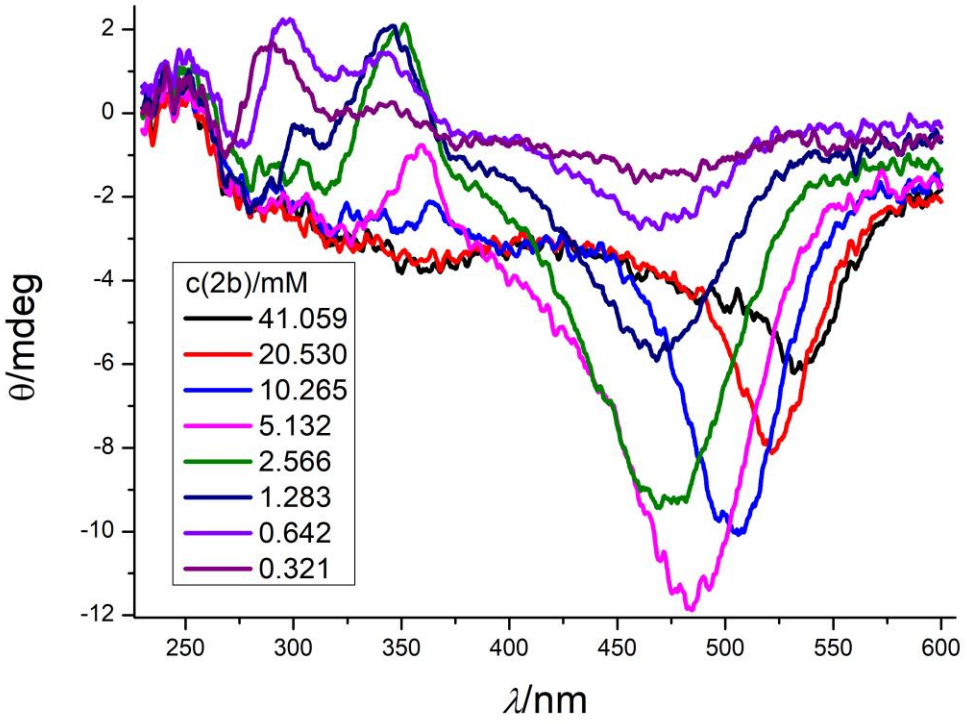
20.1 2b in DCM



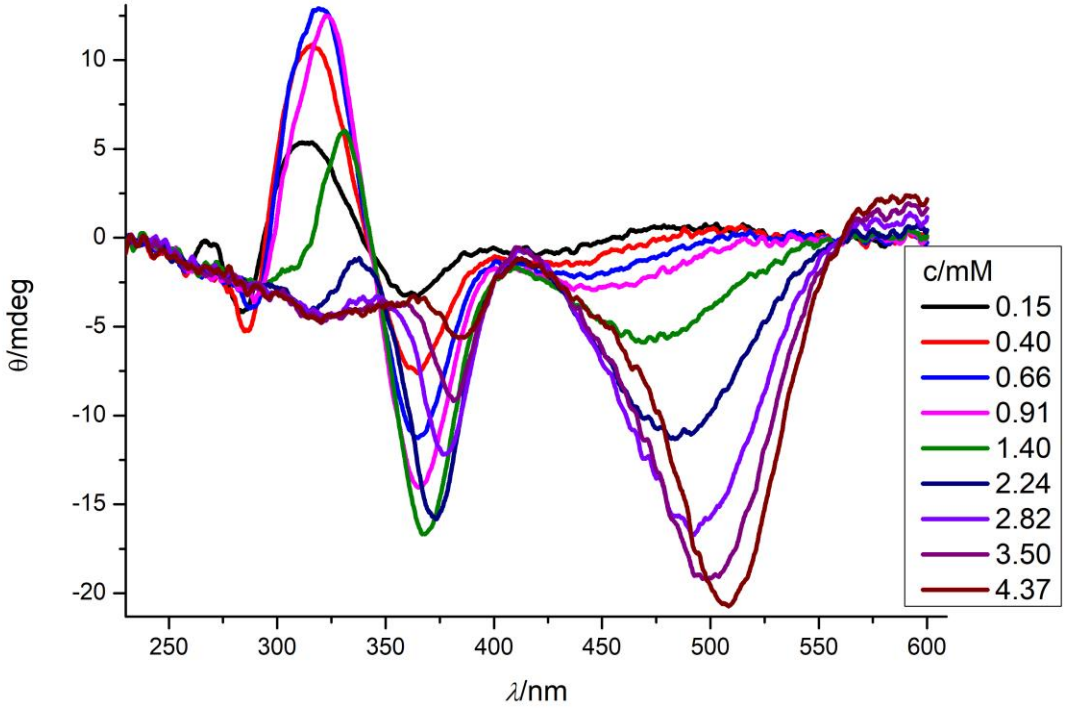
20.2 2b in MeOH



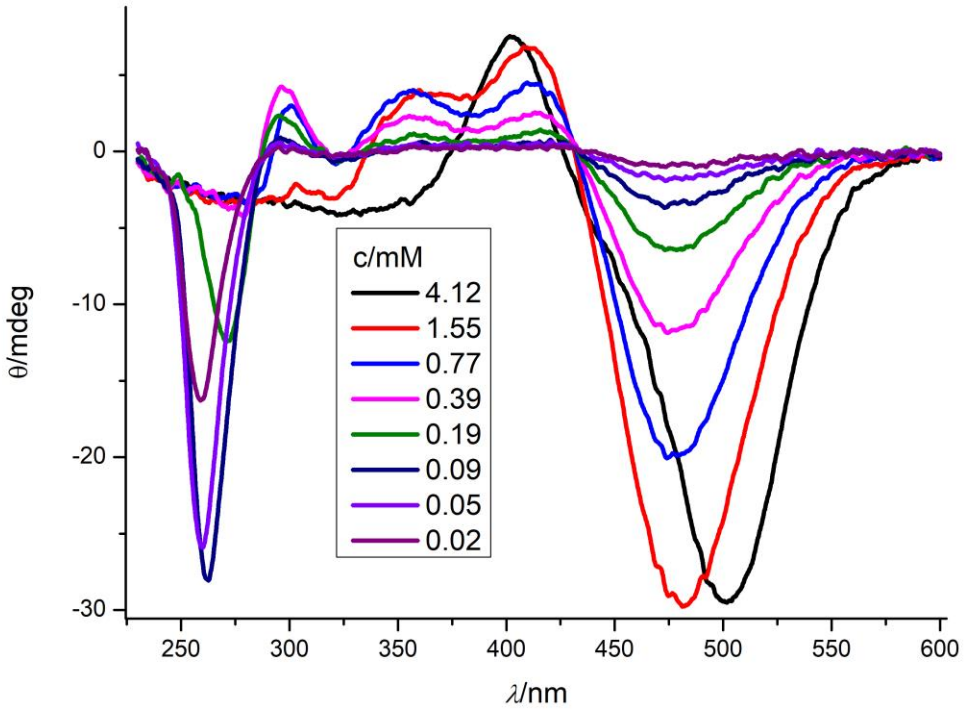
20.3 2b in DMSO



20.4 2b + 6 eq TFA



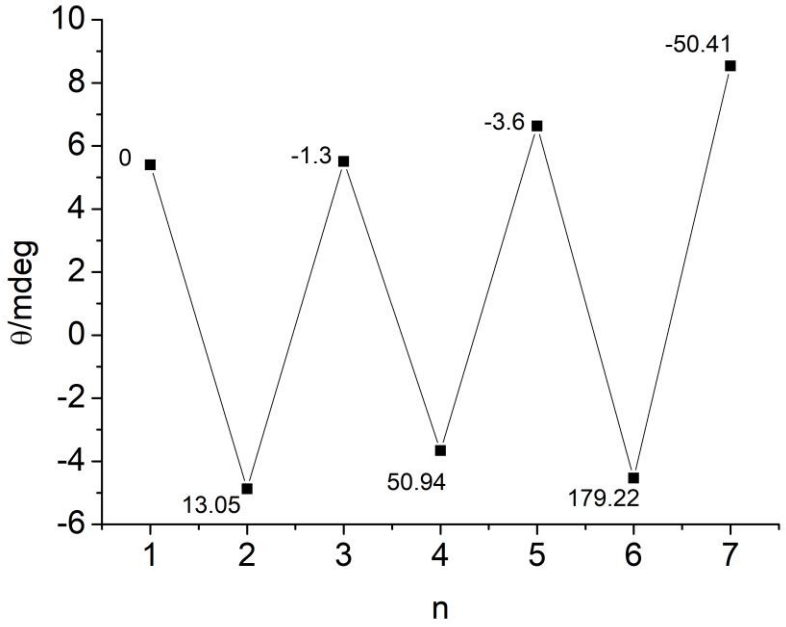
20.5 2b dilution with constant TFA concentration



c(TFA)=0.129 mM. Concentration of **2b** is shown on the graph.

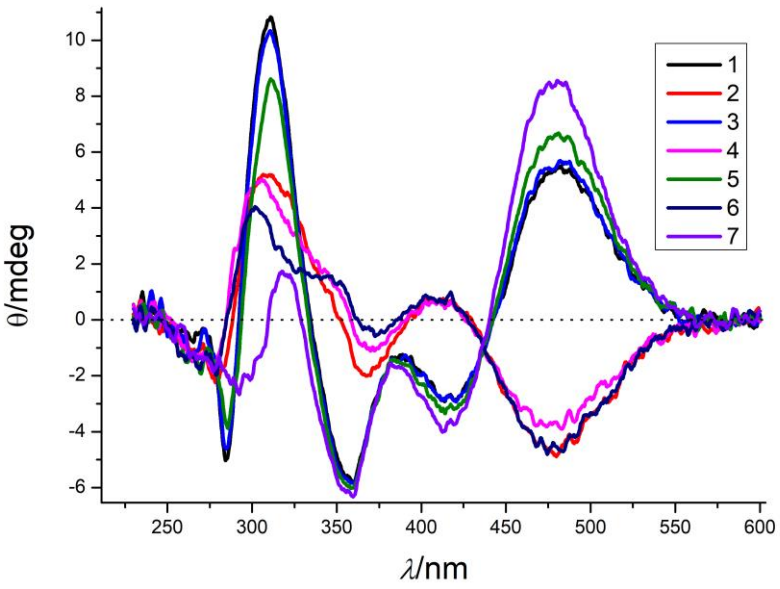
21 Tfa inversion reversibility

21.1 Reversibility at ≈ 0.35 mM



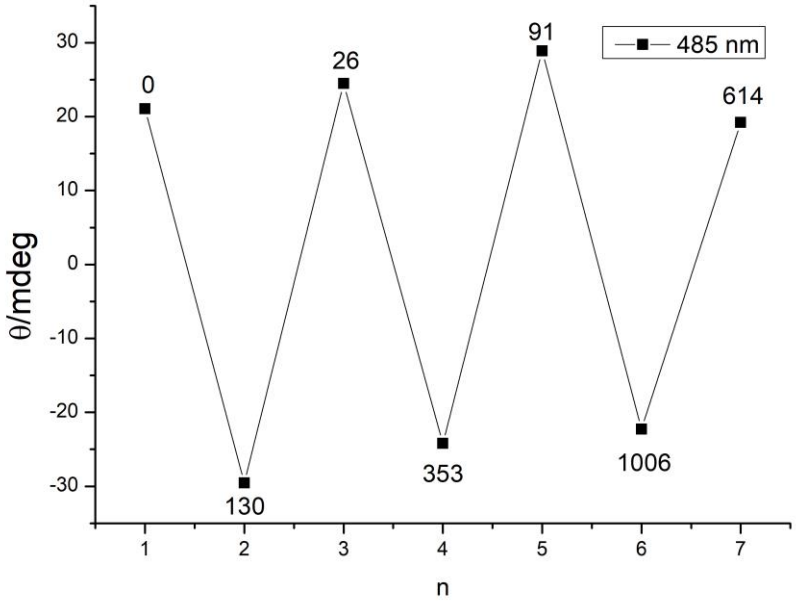
The numbers on the graph represent n(TFA)-n(DIPEA)/µmol. For each inversion cycle more and more TFA is needed for the same magnitude of change.

c(2b) = 0.37 mM – 0.34 mM



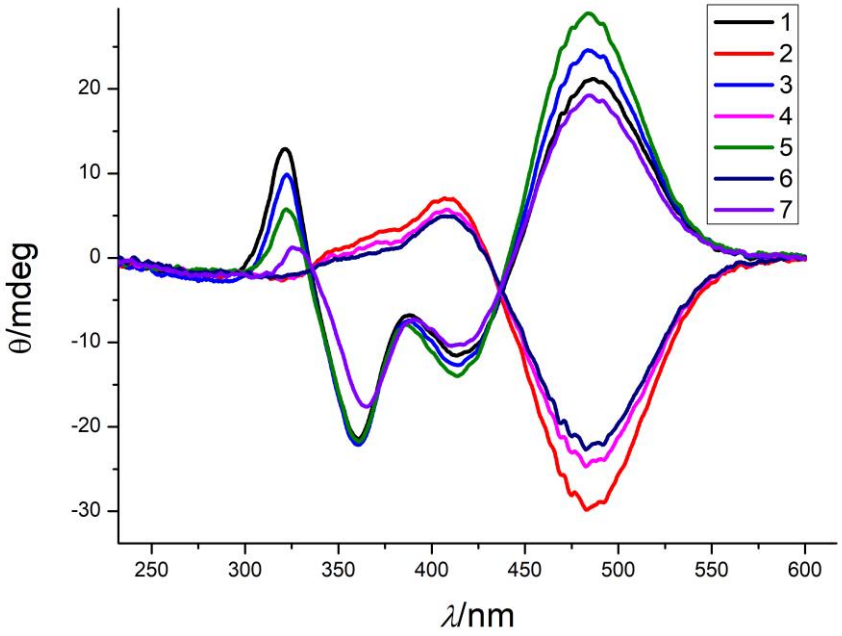
CD spectra used to generate the image above.

21.2 Reversibility at 2.13 mM



The numbers on the graph represent n(TFA)-n(DIPEA)/µmol. For each inversion cycle more and more TFA is needed for the same magnitude of change.

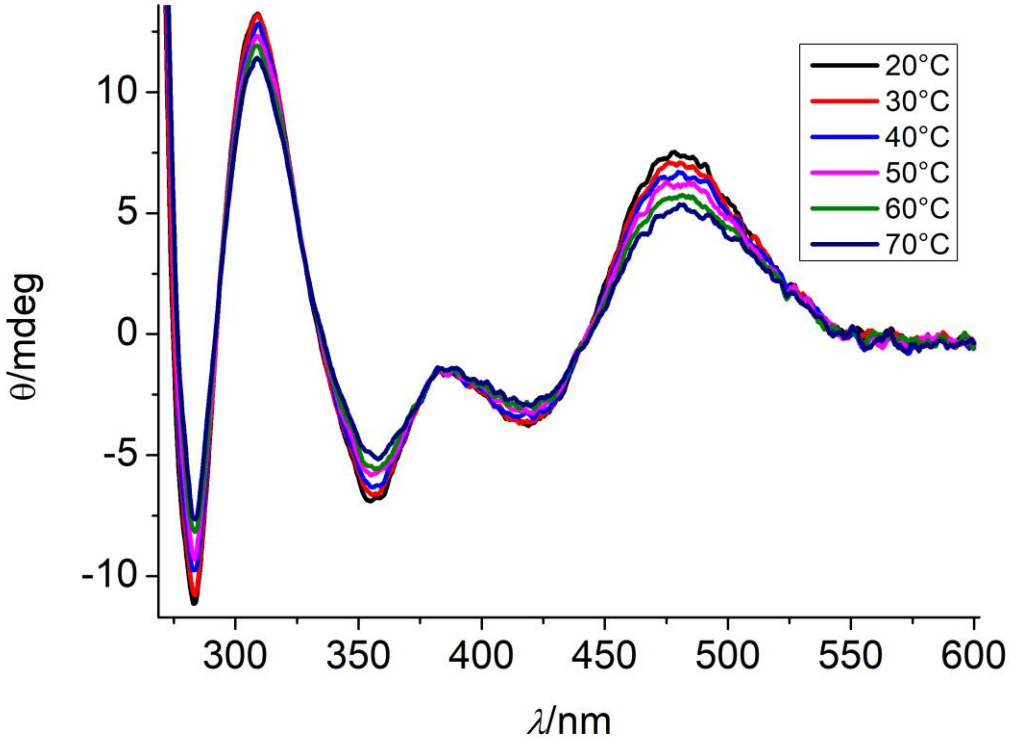
c(2b) = 2.13 mM – Experiment was done by using TFA and DIPEA solutions of **2b** of the same concentration as the measured solution, thus keeping constant concentration of the system.



CD spectra used to generate the image above.

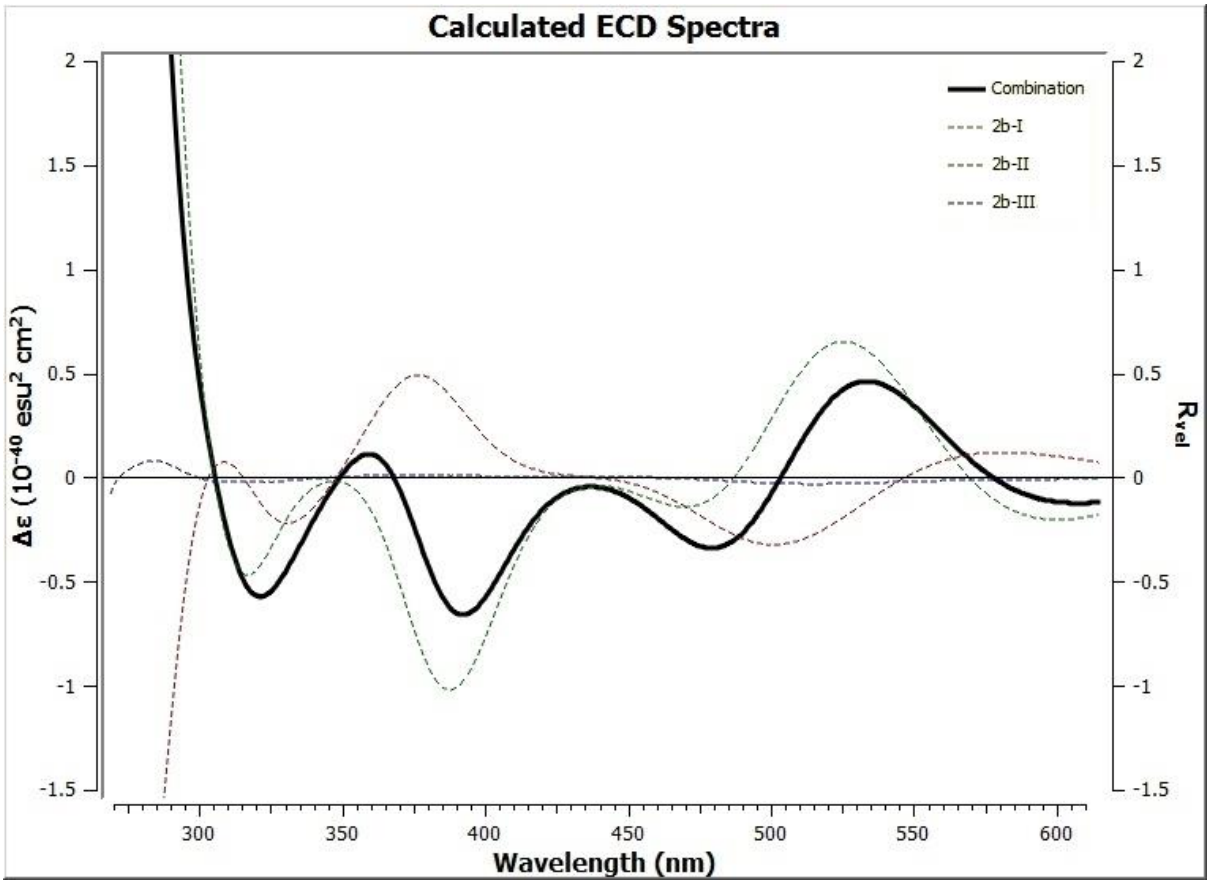
22 Temperature dependant CD spectra

22.1 2b



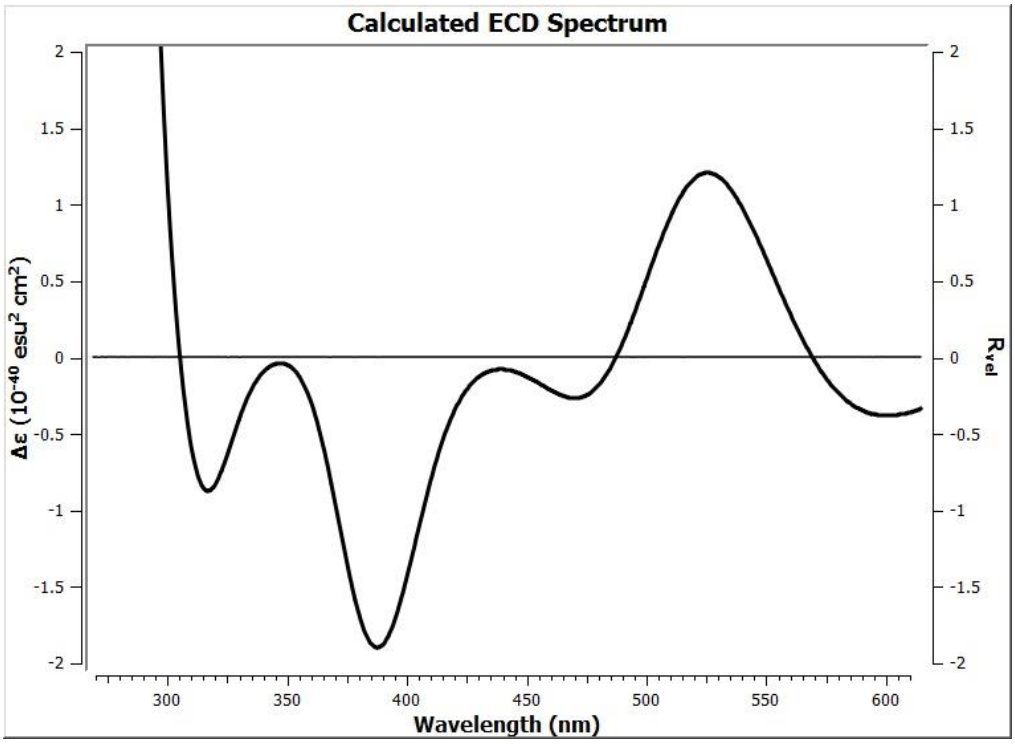
23 Calculated CD spectra

23.1 2b-I, 2b-II and 2b-III



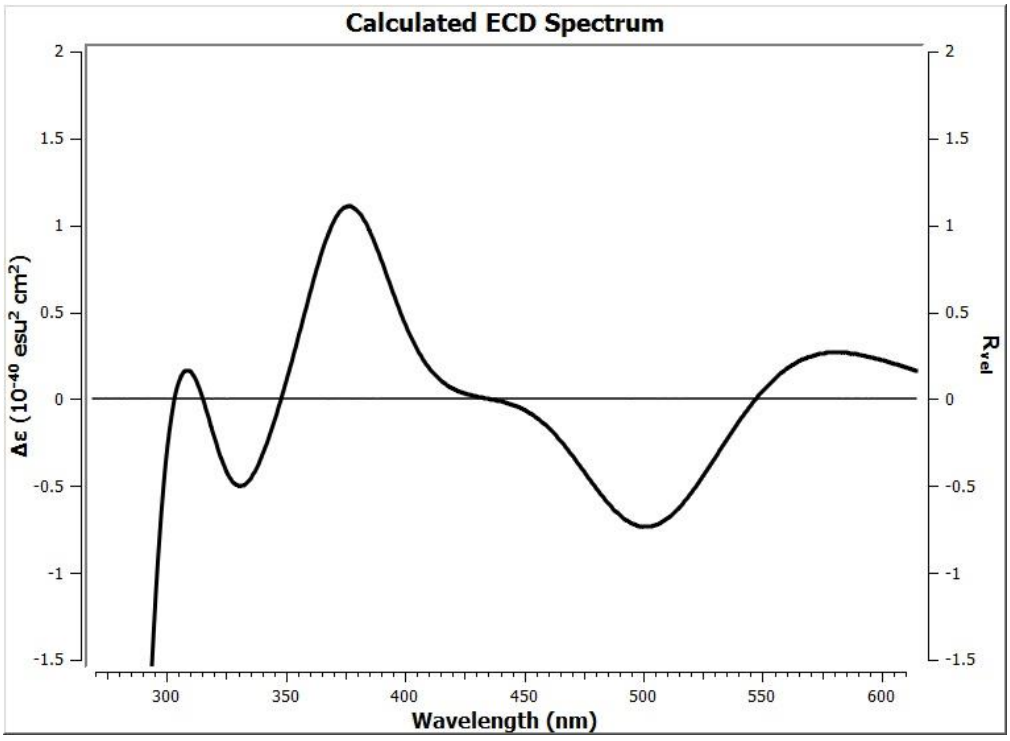
Calculated combination of ECD spectra of **2b-I**, **2b-II** and **2b-III** (in DCM), weighted by the Boltzmann population factors from the calculated Gibbs energies. The weighted contributions from **2b-I**, **2b-II** and **2b-III** are also shown.

23.2 2b-I



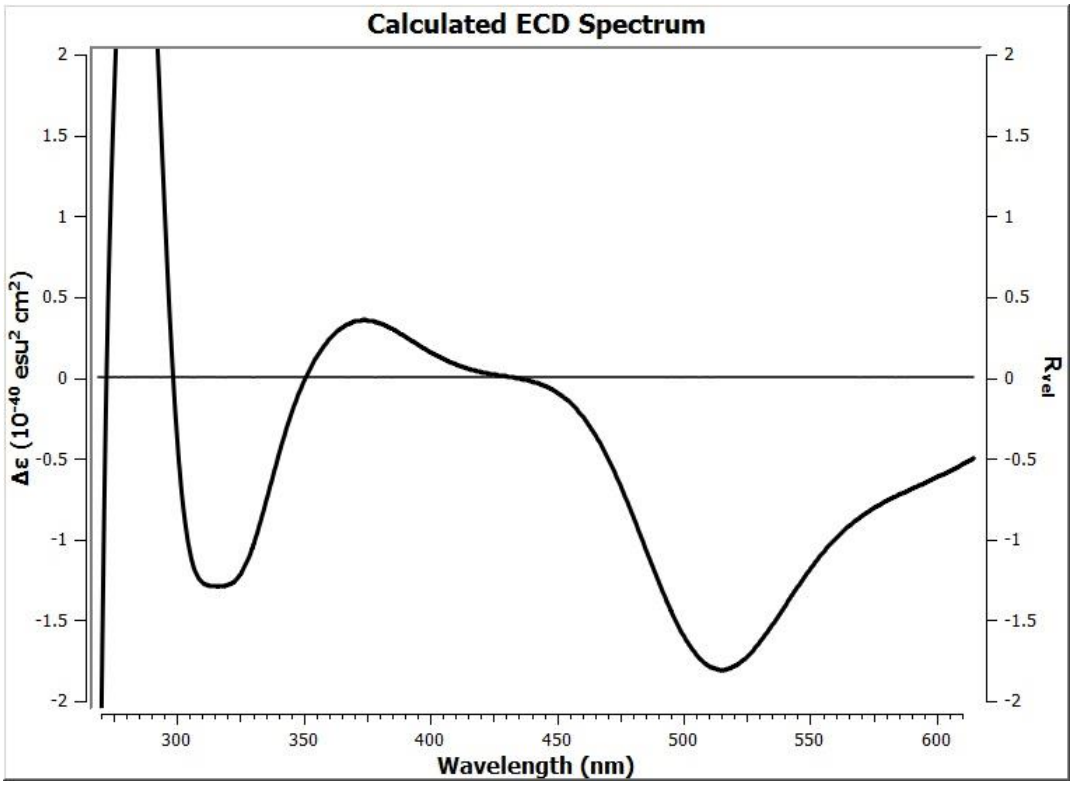
Calculated ECD spectrum of **2b-I** (in DCM)

23.3 2b-II



Calculated ECD spectrum of **2b-II** (in DCM)

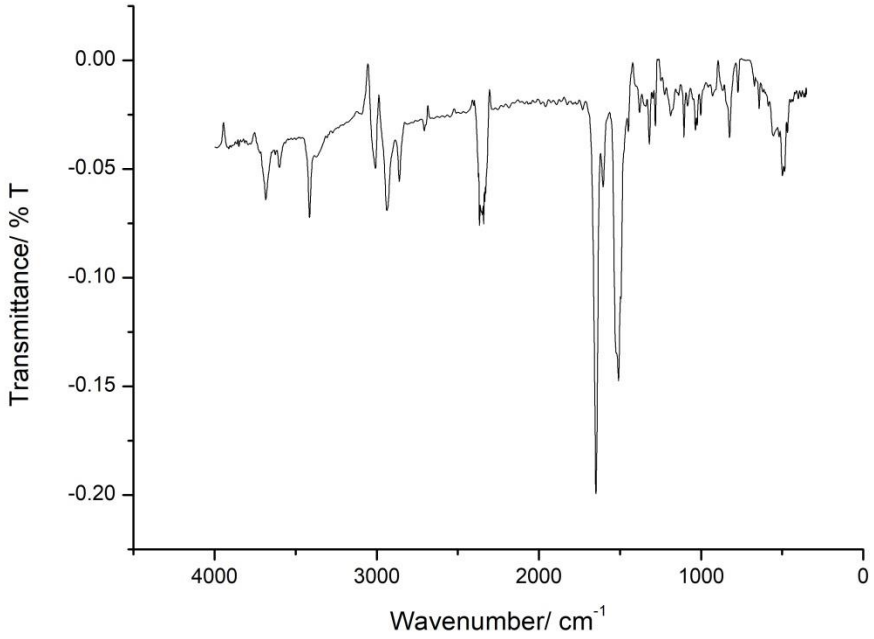
23.4 2b-III



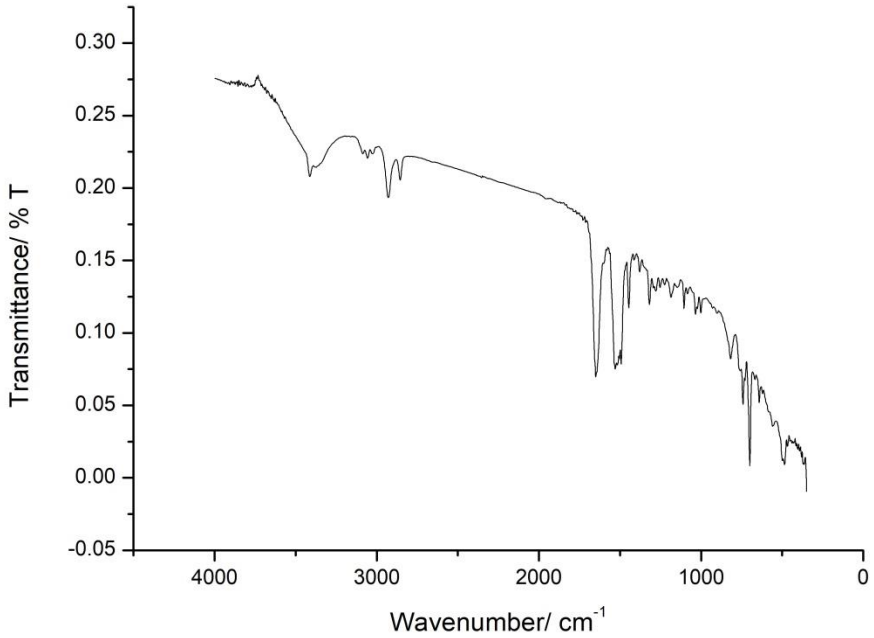
Calculated ECD spectrum of **2b-III** (in DCM).

24 Ft-IR spectra

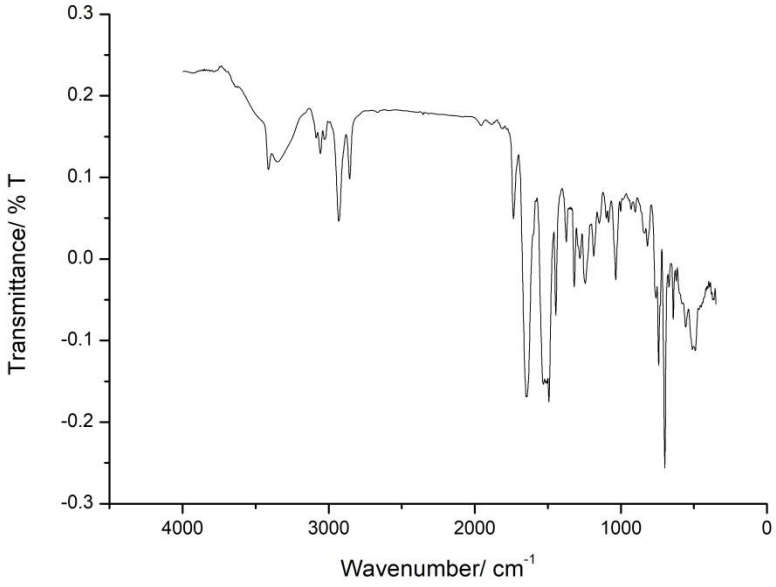
24.1 1t DCM



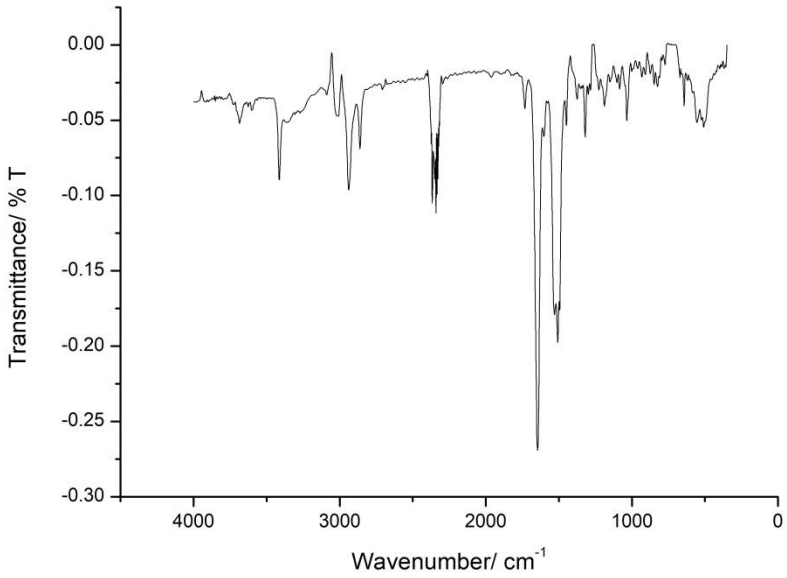
24.2 1t KBr



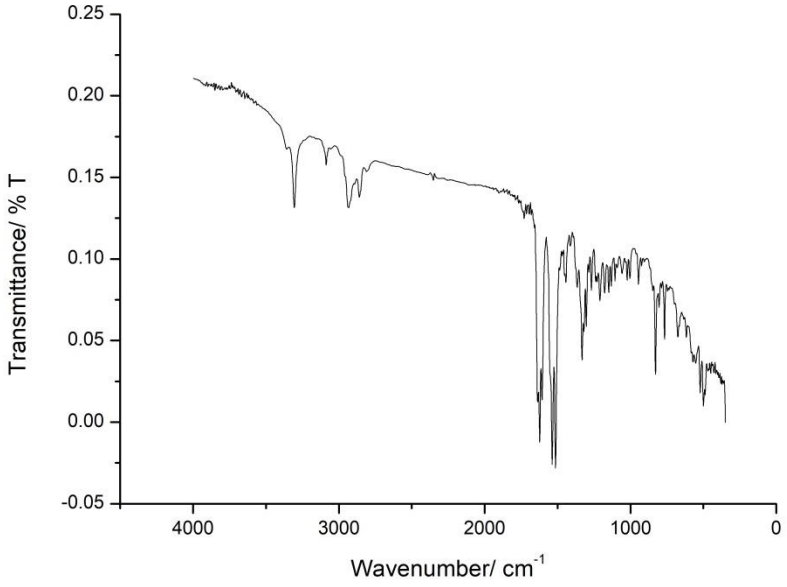
24.3 2t KBr



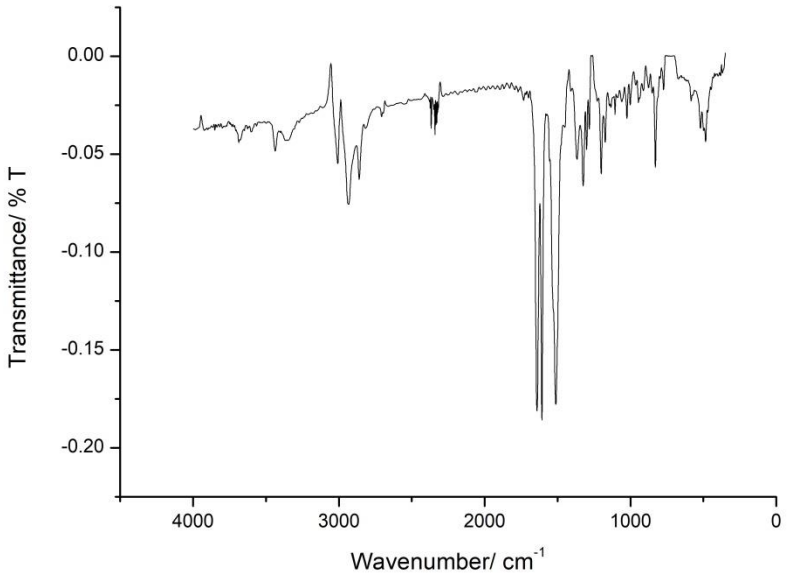
24.4 2t DCM



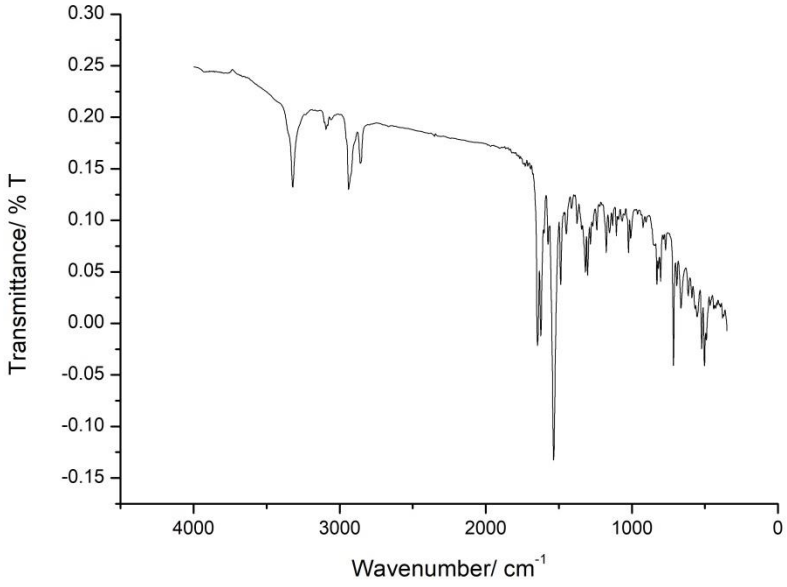
24.5 1n KBr



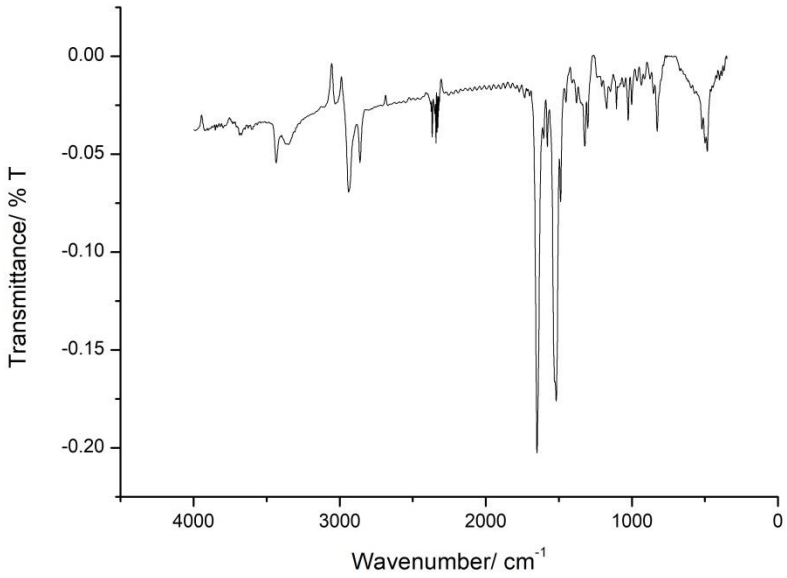
24.6 1n DCM



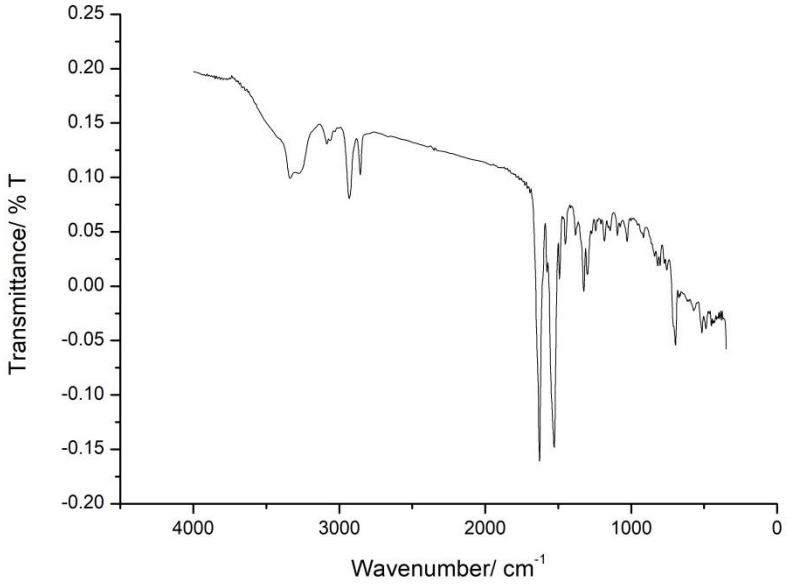
24.7 1b KBr



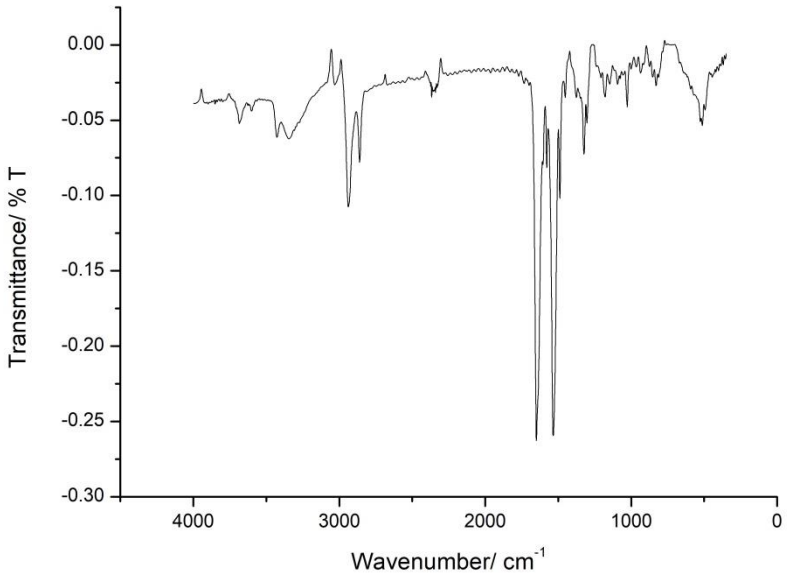
24.8 1b DCM



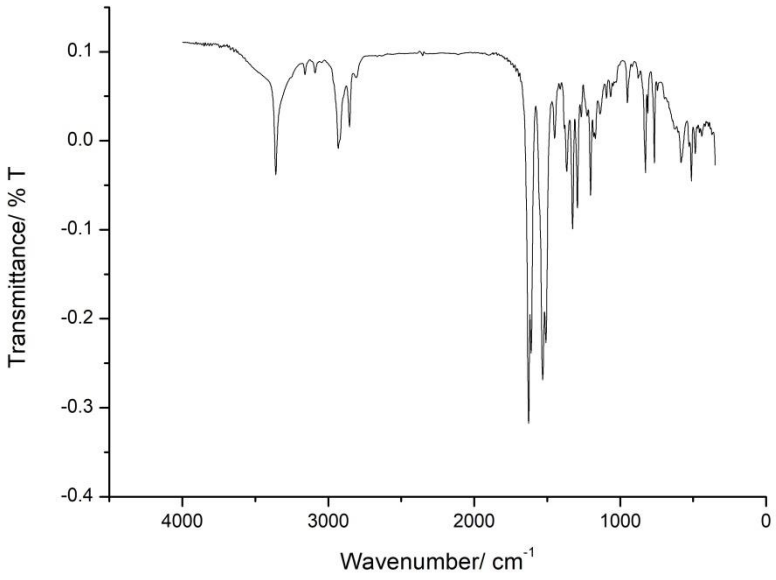
24.9 2b KBr



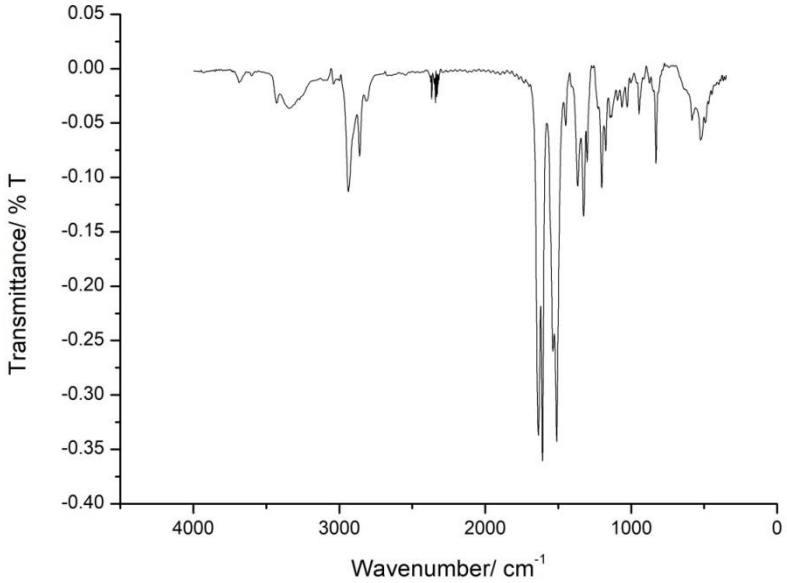
24.10 2b DCM



24.11 2n KBr



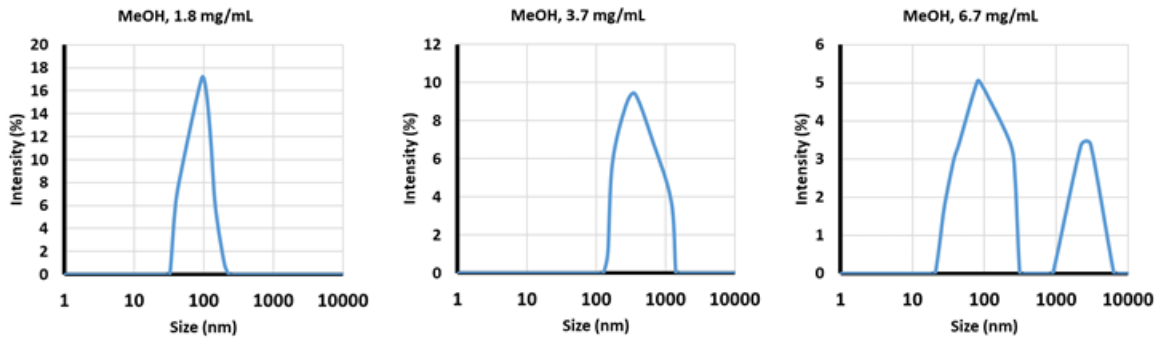
24.12 2n DCM



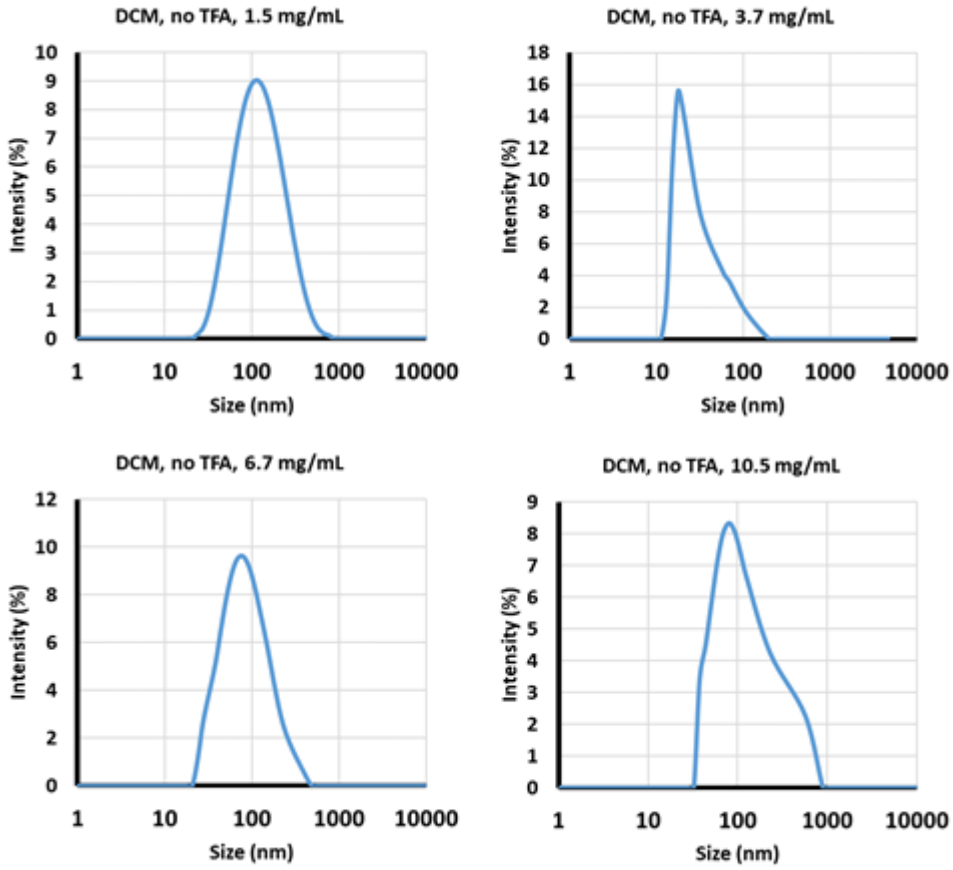
25 Dynamic light scattering (DLS)

Hydrodynamic size (d_H in nm) distribution, diffusion coefficients (D, m^2s^{-1}) and polydispersity index (PDI) of different concentrations of **2b** in DCM or MeOH with or without the addition of TFA obtained by using dynamic light scattering (DLS) technique.

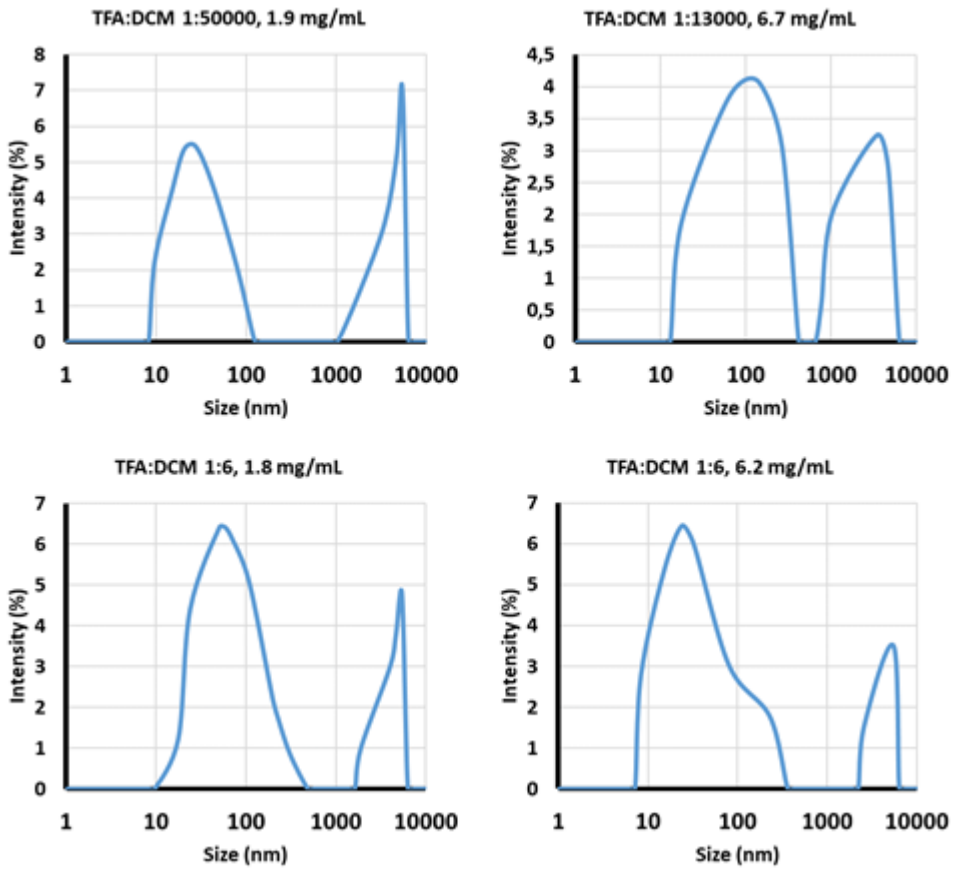
Solvent	Molar ratio 2b : TFA	[2b], mg/mL	d_H, nm (% of total particle population)	D, m^2s^{-1}	PDI
MeOH	no TFA	1.8	88.6 ± 25.6	$1.14*10^{-12} \pm 0.45*10^{-12}$	0.51 ± 0.21
	no TFA	3.7	577.2 ± 151.0	$1.23*10^{-10} \pm 0.98*10^{-10}$	0.35 ± 0.15
	no TFA	6.7	101.7 ± 32.4 (84%) 2512 ± 1113 (16%)	$2.99*10^{-10} \pm 1.82*10^{-10}$	0.43 ± 0.06
DCM	no TFA	1.5	77.2 ± 1.5	$1.12*10^{-11} \pm 0.17*10^{-11}$	0.32 ± 0.02
	no TFA	3.7	34.4 ± 20.2	$2.06*10^{-11} \pm 0.72*10^{-11}$	0.41 ± 0.29
	no TFA	6.7	89.9 ± 16.2	$1.79*10^{-11} \pm 0.86*10^{-11}$	0.59 ± 0.09
	no TFA	10.5	182.6 ± 70.5	$1.79*10^{-11} \pm 0.97*10^{-11}$	0.82 ± 0.03
	1 : 50.000	1.9	46.8 ± 35.0 (64%) 3745 ± 1210 (36%)	$8.39*10^{-11} \pm 4.52*10^{-11}$	0.53 ± 0.26
	1 : 13.000	6.7	145.2 ± 112.1 (55%) 1861 ± 286 (45%)	$5.10*10^{-11} \pm 2.82*10^{-11}$	0.56 ± 0.09
	1 : 6	1.8	84.6 ± 51.1 (76%) 4210± 966 (24%)	$4.53*10^{-11} \pm 3.56*10^{-11}$	0.52 ± 0.17
	1 : 6	6.2	101.3 ± 114.8 (75%) 4513 ± 1340 (25%)	$4.49*10^{-13} \pm 2.87*10^{-13}$	0.57 ± 0.37



Size distribution of aggregates formed after dispersing **2b** in MeOH at three different concentrations and obtained by intensity using DLS technique.



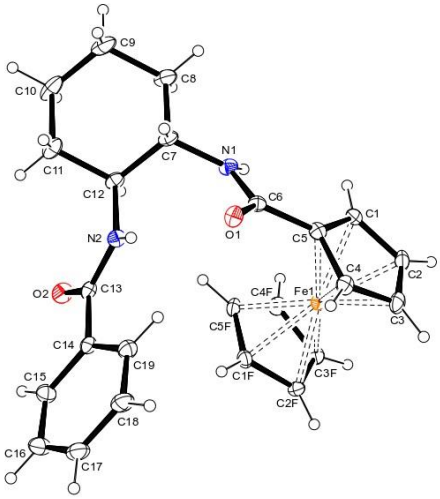
Size distribution of aggregates formed after dispersing **2b** in DCM at four different concentrations and obtained by intensity using DLS technique.



Size distribution of aggregates formed after dispersing **2b** at two different concentrations in DCM in the presence of different amounts of TFA and obtained by intensity using DLS technique.

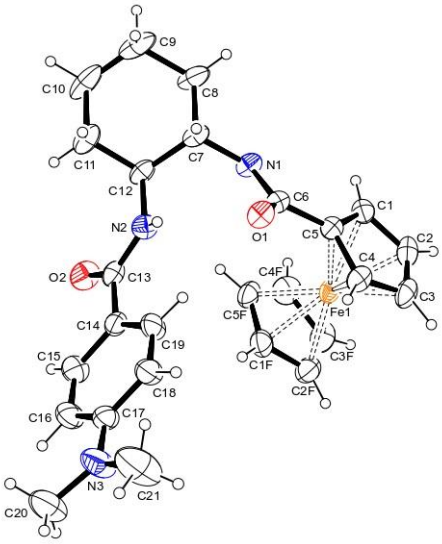
26 X-ray

26.1 1b



Molecular structure of **1b** with atom labelling scheme. Ellipsoids are drawn at 30% probability level.

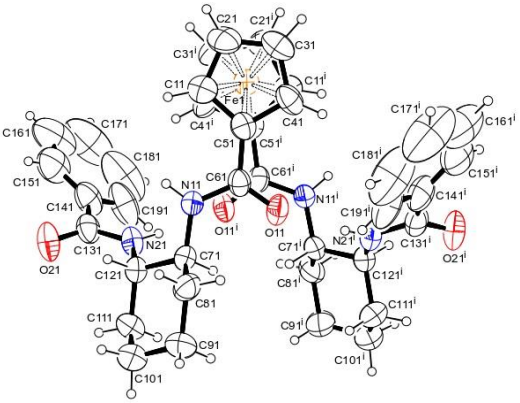
26.2 1n



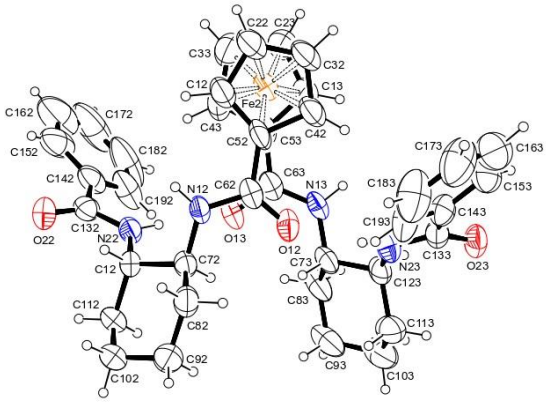
Molecular structure of **1n** with atom labelling scheme. Ellipsoids are drawn at 30% probability level.

26.3 2b and 2b*

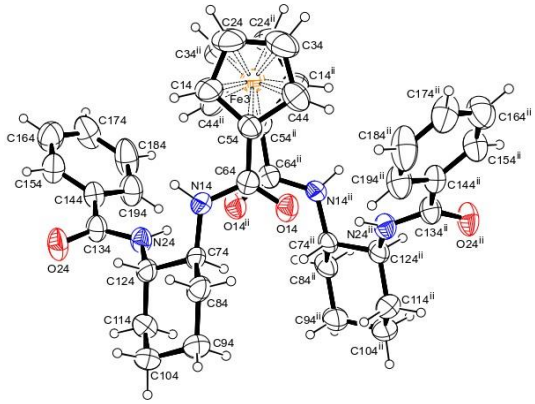
2b **2b***



1 **1**



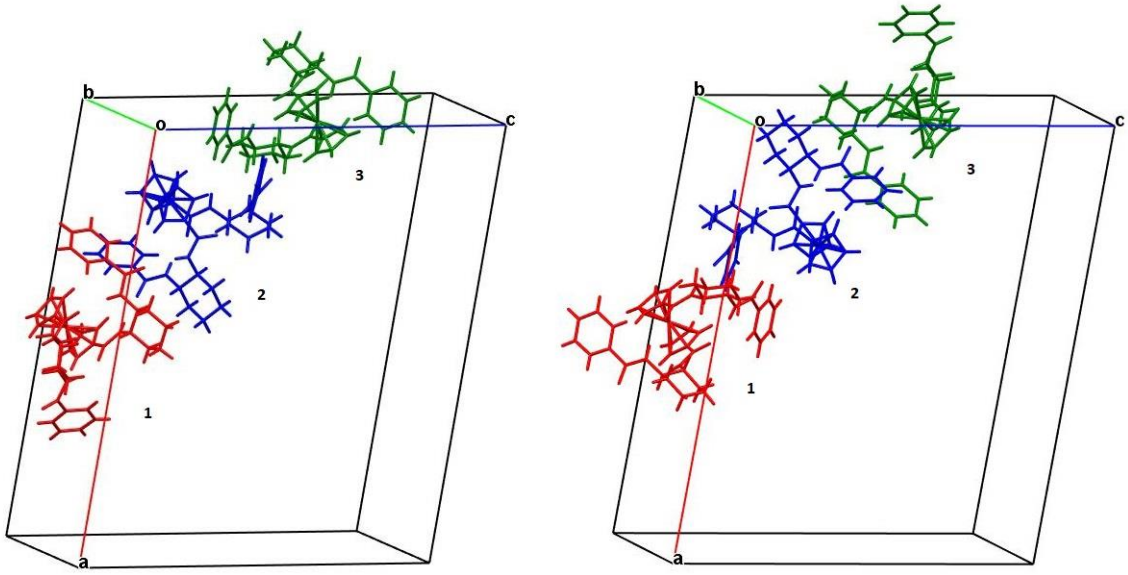
2 **2**



3 **3**

Molecular structures of individual molecules in crystal structure of **2b** (left part) and **2b*** (right part) with atom labelling scheme. Ellipsoids are drawn at 30% probability level [symmetry codes: (i): 1-*x*, *y*, -*z*; (ii): -*x*, *y*, 1-*z* (*C*2)].

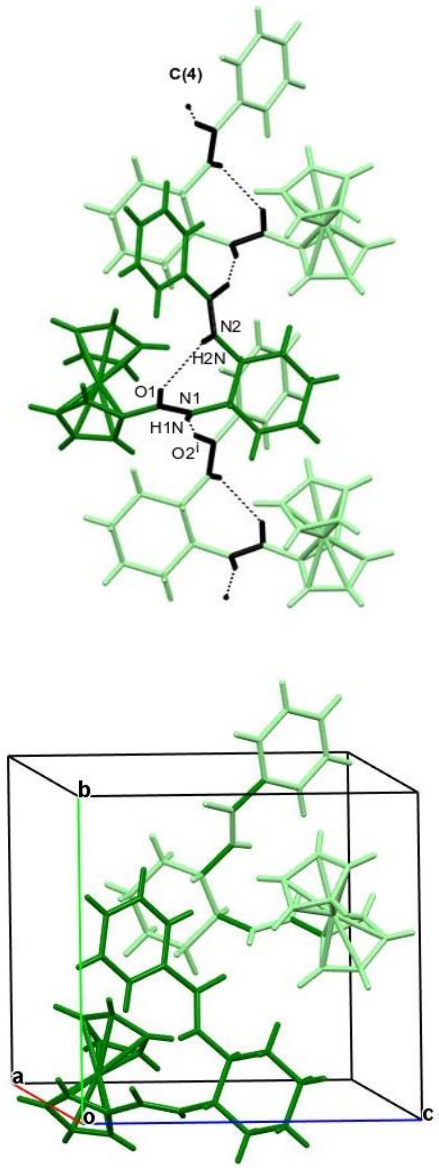
26.4 2b, 2b*independent molecule positions



2b **2b***

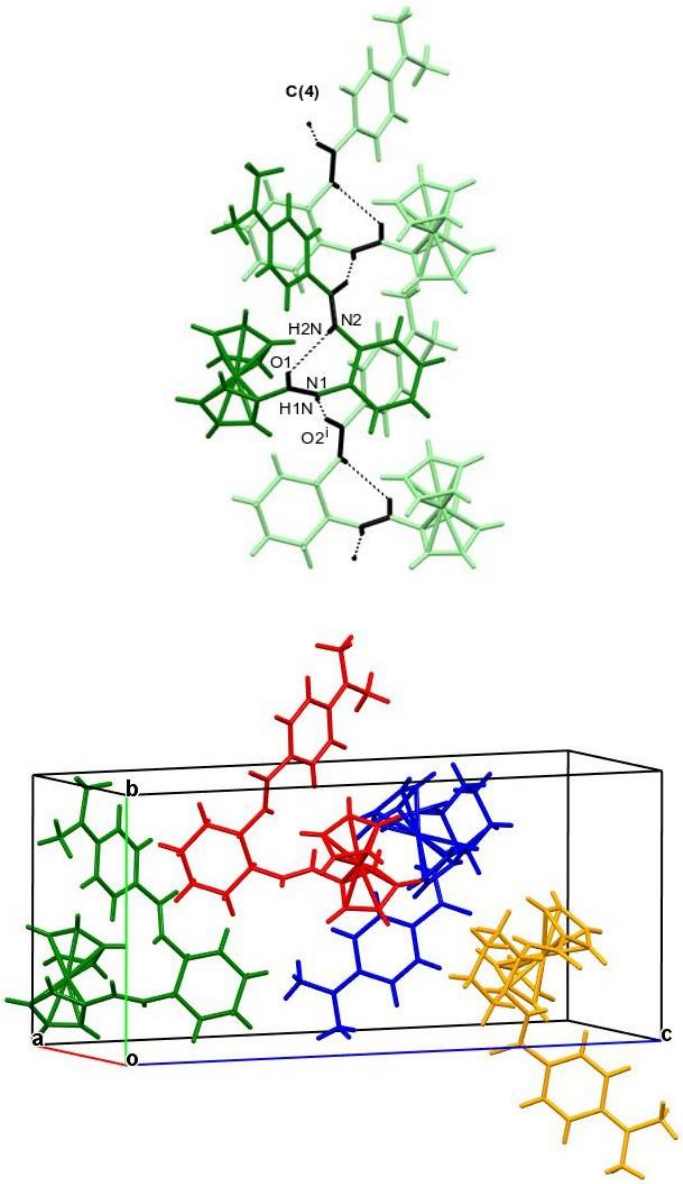
Mutual positions of molecules **1** (red) **2** (blue) and **3** (green) in crystal structure of **2b** (left part) and **2b*** (right part). Molecules **1** and **3** are positioned on 2-fold crystallographic axes and molecule **2** is positioned on general crystallographic position.

26.5 1b H-bonds and crystal packing



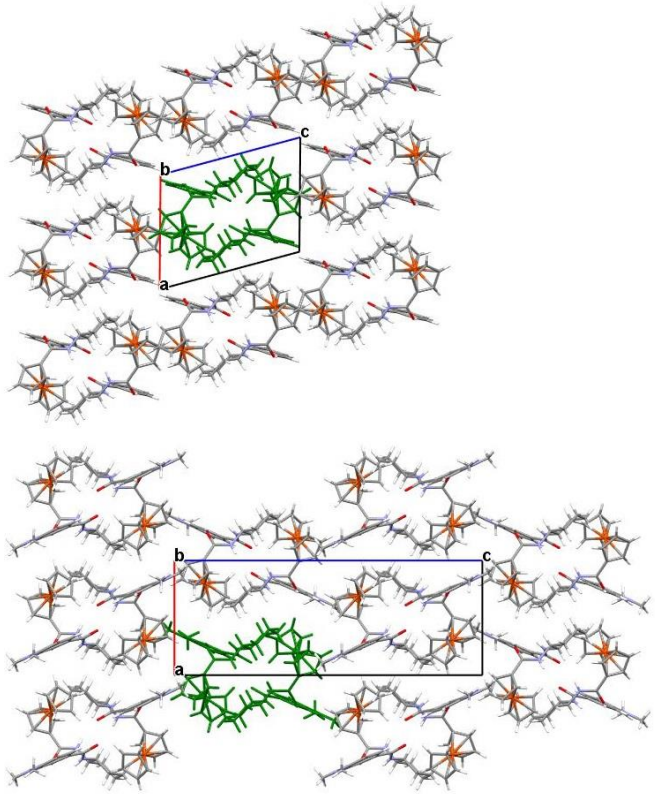
Hydrogen bonds (up) and crystal packing (bottom) in crystal structure of **1b**. One dimensional hydrogen bonding motif with graph set notation **C(4)** is highlighted in black with labelled atoms. Original asymmetric unit is dark green coloured [symmetry code (i): 1-*x*, -1/2+*y*, 1-*z* ($P2_1$)].

26.6 1n H-bonds and crystal packing



Hydrogen bonds (up) and crystal packing (bottom) in crystal structure of **1n**. One dimensional hydrogen bonding motif with graph set notation **C(4)** is highlighted in black with labelled atoms. Original asymmetric unit is dark green coloured [symmetry code (i): 2-*x*, -1/2+*y*, 1/2-*z* ($P2_12_12_1$)].

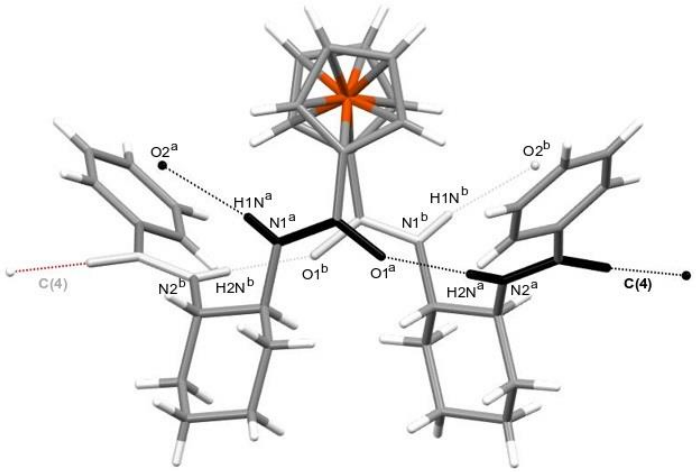
26.7 1b and 2b packing difference



1b **1n**

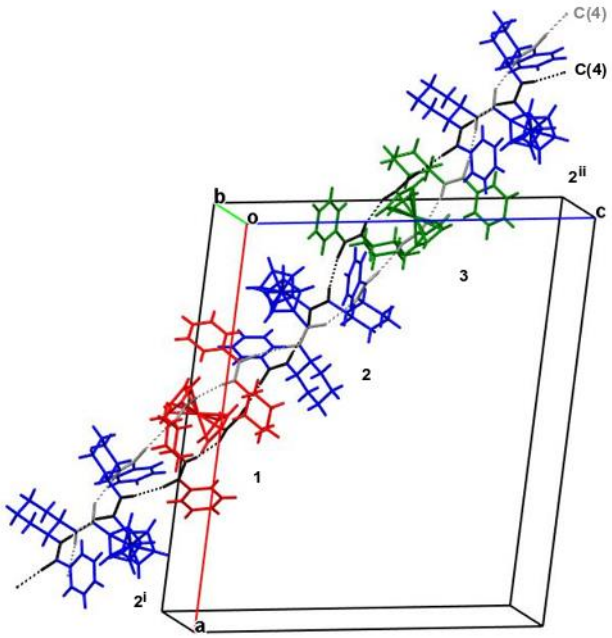
Difference in packing of one-dimensional hydrogen bonding motifs of **C(4)** graph-set notation in **1b** (left, $P2_1$ space group) and **1n** (right, $P2_12_12_1$ space group). Views on the structures are along *b* crystallographic axes and one of hydrogen bonding motifs is highlighted by green colour.

26.8 Hydrogen bonding in 2b – single molecule



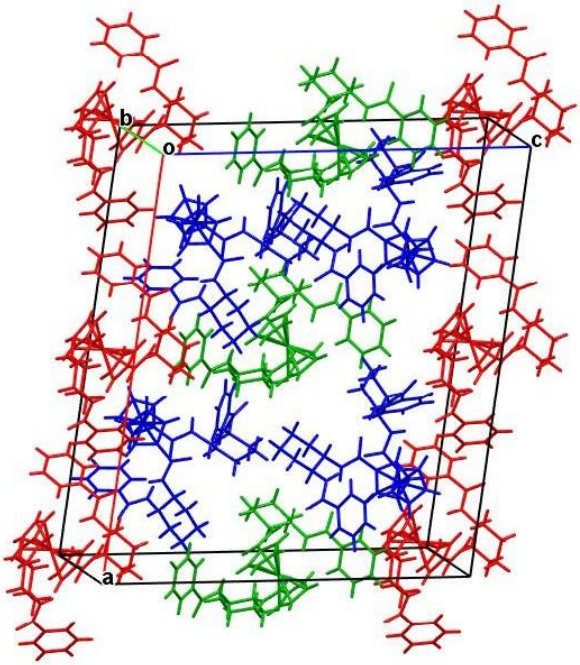
One representative molecule for structure **2b**, showing basic hydrogen bonding motif common for all symmetry independent molecules **1**, **2** and **3**. Same motif is valid for **2b*** where motif is opposite enantiomer of that shown in figure. Labels are different for particular molecules **1**, **2** and **3**: $N1^{a}$, $H1N^{a}$, $O2^{a}$, $N2^{a}$, $H2N^{a}$, $O1^{a}$, $N1^{b}$, $H1N^{b}$, $O2^{b}$, $N2^{b}$, $H2N^{b}$ and $O1^{b}$ labels are $N11^{i}$, $H11N^{i}$, $O22^{i}$, N21, H21N, $O11^{i}$, N11, H11N, O22, $N21^{i}$, $H21^{i}$ and O11 for **1**, respectively, N12, H12N, O21, N23, H23N, O12, N13, H13N, O24, N22, H22N and O13 for **2**, respectively and N14, H14N, O23, $N24^{ii}$, $H24^{ii}$, O14, $N14^{ii}$, $H14^{ii}$, $O23^{ii}$, N24, H24N and $O14^{ii}$ for **3**, respectively [symmetry codes: (i): 1-*x*, *y*, -*z*; (ii): -*x*, *y*, 1-*z* (*C*2)]. All symmetry independent hydrogen bonds and their geometry parameters are listed in **Table 22.15**. Basic hydrogen bonding motif consist of two one-dimensional amide-amide motifs of graph set notation **C(4)**, emphasized in black and light grey colour.

26.9 Hydrogen bonding in 2b – motif

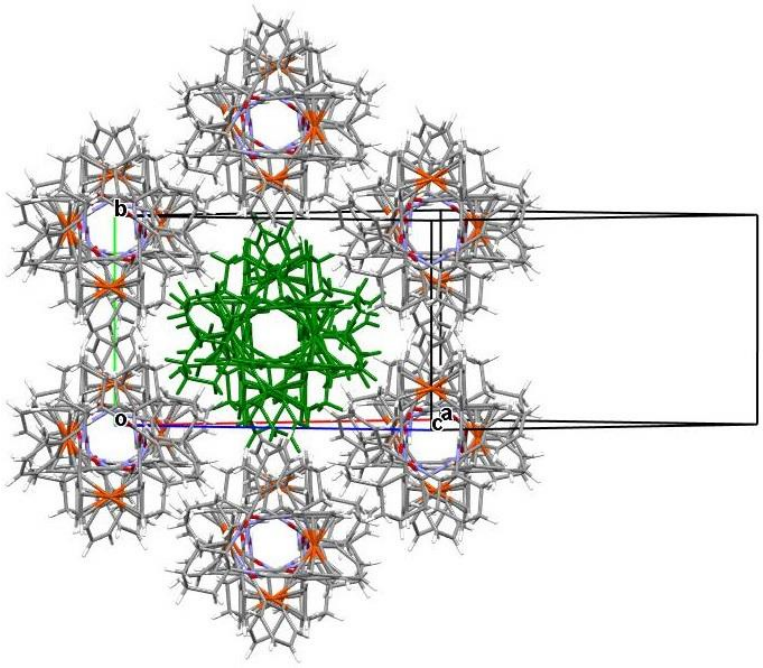


Complete hydrogen bonded one-dimensional motif (chain of molecules **1**, **2** and **3**) in **2b** formed by two strands of amide-amide chain motifs of **C(4)** graph set notation emphasized in black and grey. Chain extrudes along one of the face diagonals of the unit cell, *i.e.* along direction {-1, 0 1} [symmetry codes: (i): 1-*x*, *y*, -*z*; (ii): -*x*, *y*, 1-*z* (*C*2)].

26.10 2b crystal packing



a)



b)

a) Crystal packing of molecules in one unit cell for **2b**. b) Packing of one-dimensional hydrogen bonded chains of molecules shown in , viewing along their direction of propagation. One chain is emphasized in green colour. Picture emphasize hexagonal surrounding of one chain in the structure.

26.11 Experimental data for the X-ray diffraction studies.

Compound	**1b**	**1n**	**2b** [2b*]
Formula	$C_{24}H_{26}FeN_2O_2$	$C_{26}H_{31}FeN_3O_2$	$C_{38}H_{42}FeN_4O_4$+solvent
F_w (g mol^{-1})	430.32	473.39	674.61
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1$	$P2_12_12_1$	$C2$
a (Å)	8.8082(2)	8.9319(2)	27.994(2) [27.846(2)]
b (Å)	10.9118(2)	11.0143(3)	11.178(1) [11.1554(6)]
c (Å)	11.1489(2)	24.0525(7)	24.045(3) [23.762(2)]
α (°)	90	90	90
β (°)	105.480(2)	90	96.91(1) [97.506(7)]
γ (°)	90	90	90
V (Å^3)	1032.69(3)	2366.25(11)	7469.1(14) [7318.0(9)]
Z	2	4	8
D_{calc} (g cm^{-3})	1.384	1.329	1.200 [1.225]
F(000)	452	1000	2848
Radiation (Å)	1.54184	1.54184	1.54184
Temperature (K)	128(5)	293(2)	293(2) [114(12)]
Reflections collected	5162	6654	11617 [15097]
Independent reflections	3538	3978	8855 [6005]
R_{init}	0.0346	0.0486	0.0286 [0.0944]
Reflections observed	3444	3183	5078 [3333]
Parameters	270	299	848 [836]
Flack parameter	-0.011(4)	-0.014(5)	-0.013(6) [-0.006(9)]
R_1 [$I > 2\sigma(I)$][a]	0.0353	0.0466	0.0541 [0.0698]
wR_2 (all data)[b]	0.0933	0.1124	0.1325 [0.1562]
Goof, S[c]	1.041	1.079	0.986 [0.975]
Maximum/minimum electron density (e Å^3)	0.388/ -0.339	0.285/-0.450	0.157/-0.193 [0.242/-0.205]

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ where n is number of reflections and p is the total number of parameters refined.

26.12Selected bond lengths and angles for 1b, 1n and 2b [2b*].

	1b	1n	2b [2b*] [a]
Bond lengths (Å)			
<C–C>$_{Ferrocene}$	1.425(8)	1.41(1)	1.41(2) [1.42(2)]
<Fe–C>$_{Ferrocene}$	2.042(3)	2.04(2)	2.04(2) [2.04(2)]
C5–C6	1.481(5)	1.490(7)	1.477(12), 1.493(11), 1.482(12), 1.452(11) [1.478(19), 1.46(2), 1.465(19), 1.50(2)]
C6–O1	1.246(5)	1.234(6)	1.226(9), 1.233(9), 1.252(8), 1.232(8) [1.253(15), 1.277(18), 1.220(15), 1.245(17)]
C6–N1	1.346(5)	1.351(6)	1.344(9), 1.353(8), 1.340(10), 1.348(8) [1.358(16), 1.362(19), 1.387(17), 1.329(17)]
N1–C7	1.461(5)	1.449(7)	1.445(10), 1.454(9), 1.456(10), 1.447(9) [1.455(14), 1.452(16), 1.471(15), 1.467(16)]
<C–C>$_{Cyclohexane}$	1.527(5)	1.52(1)	1.522(1) [1.52(2)]
C12–N2	1.463(4)	1.461(7)	1.444(11), 1.446(10), 1.462(11), 1.465(9) [1.471(15), 1.456(15), 1.448(15), 1.46(2)]
N2–C13	1.333(5)	1.340(7)	1.332(10), 1.344(10), 1.351(10), 1.333(9) [1.298(16), 1.349(17), 1.362(18), 1.38(2)]
C13–O2	1.241(4)	1.228(6)	1.235(10), 1.238(9), 1.244(9), 1.241(8) [1.252(17), 1.262(16), 1.230(19), 1.24(2)]
C13–C14	1.498(5)	1.496(7)	1.500(14), 1.472(14), 1.484(13), 1.488(11) [1.50(2), 1.50(2), 1.50(3), 1.47(3)]
<C–C>$_{Benzene}$	1.391(5)	1.39(1)	1,37(2) [1.38(2)]
C17–N3		1.375(7)	
<N3–C_{Methyl}>		1.433(6)	
Bond angles (°)			
<C–C–C >$_{Ferrocene}$	108.0(5)	108.0(9)	108(1) [108(2)]
<C–Fe–C >$_{Ferrocene}$ [b]	107.9(9)	108(2)	108(1) [108(1)]
C1–C5–C6	129.1(3)	129.1(5)	128.1(8), 129.7(7), 127.3(8), 130.0(7) [129.2(15), 125.2(19), 131.3(16), 126.4(17)]
C5–C6–N1	117.5(3)	116.8(5)	117.4(8), 115.8(8), 118.7(7), 116.6(7) [116.1(15), 119.4(18), 114.1(15), 117.8(16)]
C6–N1–C7	122.2(3)	123.0(5)	121.0(7), 121.4(6), 122.4(6), 120.5(6) [121.1(12), 122.4(15), 119.3(13), 121.0(13)]
N1–C7–C8	109.1(3)	109.6(4)	112.0(8), 112.6(7), 111.9(8), 112.5(7) [112.0(11), 111.0(12), 112.0(11), 111.9(13)]
<C–C–C >$_{Cyclohexane}$	111.0(2)	111.0(5)	110.8(9) [111(1)]
C11–C12–N2	110.5(3)	111.4(5)	111.8(9), 111.5(7), 109.6(9), 112.3(8) [113.5(12), 112.2(12), 109.9(10), 110.5(16)]
C12–N2–C13	123.7(3)	124.5(5)	120.5(7), 121.2(7), 122.6(7), 120.4(6) [119.0(14), 122.8(14), 122.7(14), 123.7(19)]
N2–C13–C14	117.0(3)	115.3(5)	117.0(9), 116.0(8), 117.8(8), 117.8(6) [117.1(17), 119.4(16), 116.8(19), 117(2)]
C13–C14–C15	118.3(3)	118.9(5)	119.7(12), 119.2(12), 117.9(10), 118.7(7) [120.4(18), 117.8(18), 116(2), 117(2)]
<C–C–C >$_{Benzene}$	120.0(8)	120(3)	120(1) [120(2)]
C16–C17–N3		121.9(5)	
C20–N3–C21		118.5(7)	

[a] For averaged bond and angles represented by < > brackets, the mean value of bonds and angles in all 3 symmetry independent molecules are given, for individual bonds and angles the values of four symmetry independent bond and angles are given in the row (C51-C61, C52-C62, C53-C63, C54-C64 for C5-C6, etc.)

[b] Angles are taken between carbon atoms which are eclipsed one above the other, with Fe atom in the vertex (C5–Fe1–C5F, etc.).

26.13 Selected torsion angles (°) for 1b, 1n and 2b [2b*].

Torsion angle	1b	1n	2b [2b*]
C6–C5···C5F–H5F	~19	~18	
C61–C51···C51^{i}–C61^{i}			-11.39(1) [10.26(1)]
C62–C52···C53–C63			-14.27(1) [13.86(1)]
C64–C54···C54^{ii}–C64^{ii}			-11.48(1) [9.97(1)]
C1–C5–C6–O1	−170.9(4)	−165.9(5)	
C11–C51–C61–O11			178.4(7) [179.4(14)]
C12–C52–C62–O12			176.8(11) [-179.4(16)]
C13–C53–C63–O13			179.0(10) [-179.0(18)]
C14–C54–C64–O14			177.1(8) [-178.1(15)]
C6–N1–C7–C12	−87.4(4)	−87.6(6)	
C61–N11–C71–C121			-147.9(7) [151.2(13)]
C62–N12–C72–C122			-149.2(8) [149.4(13)]
C63–N13–C73–C123			-151.2(8) [149.2(12)]
C64–N14–C74–C124			-151.9(6) [146.9(15)]
C7–C12–N2–C13	−160.5(3)	−163.3(5)	
C71–C121–N21–C131			-149.9(8) [149.9(12)]
C72–C122–N22–C132			-154.4(7) [153.1(13)]
C73–C123–N23–C133			-154.7(7) [154.4(13)]
C74–C124–N24–C134			-149.9(7) [148.4(17)]
O2–C13–C14–C15	−13.9(5)	−12.6(9)	
O21–C131–C141–C151			34.8(16) [-26(2)]
O22–C132–C142–C152			24.1(13) [-26(2)]
O23–C133–C143–C153			26.7(13) [-26(3)]
O24–C134–C144–C154			23.7(13) [-36(3)]
C16–C17–N3–C20		-6.1(12)	

26.14Hydrogen bond parameters for 1b and 1n.

	1b	**1n**
parameter	N1-H1N···O2[i]	
N-H (Å)	0.88(6)	0.76(5)
H···O (Å)	2.12(6)	2.22(5)
N···O (Å)	2.973(4)	2.964(6)
N-H···O (°)	162(6)	167(5)
	N2-H2N···O1 (intra)	
N-H (Å)	0.78(6)	0.76(7)
H···O (Å)	2.32(6)	2.40(7)
N···O (Å)	2.898(4)	2.907(6)
N-H···O (°)	132(5)	126(7)

Symmetry code: (i): 1-*x*, -1/2+*y*, 1-*z* for **1b** ($P2_1$), 2-*x*, -1/2+*y*, 1/2-*z* for **1n** ($P2_12_12_1$)

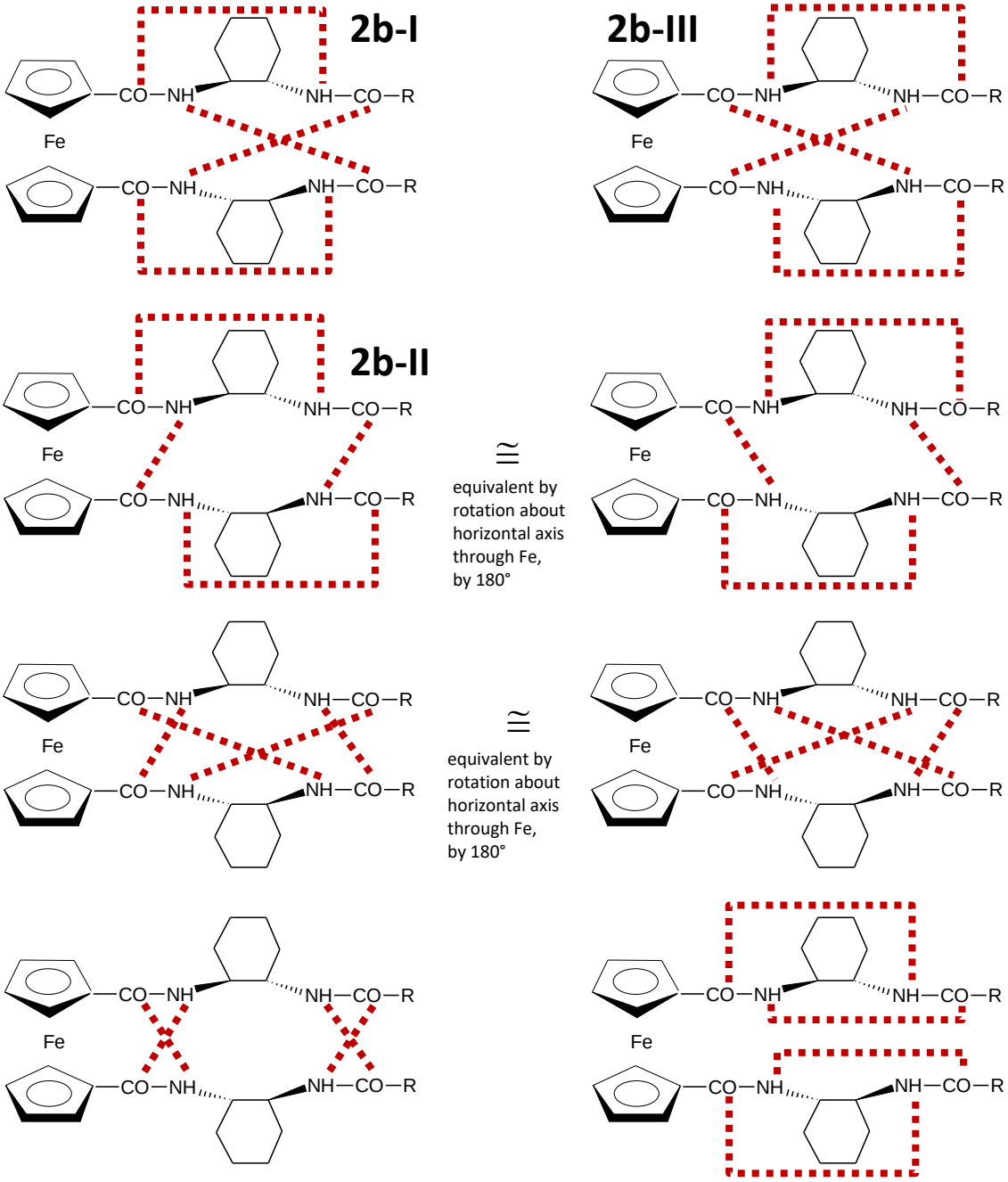
26.15 Hydrogen bond parameters for 2b and 2b*.

	2b	**2b***
parameter	N11-H11N···O22	
N-H (Å)	0.86	0.86
H···O (Å)	2.18	2.14
N···O (Å)	3.017(8)	2.980(16)
N-H···O (º)	166	167
	N21-H21N···O11^{i} (intra)	
N-H (Å)	0.86	0.86
H···O (Å)	2.03	2.03
N···O (Å)	2.875 (8)	2.871(16)
N-H···O (º)	168	166
	N12-H12N···O21	
N-H (Å)	0.86	0.86
H···O (Å)	2.18	2.14
N···O (Å)	3.025 (8)	2.981(17)
N-H···O (º)	169	168
	N22-H22N···O13 (intra)	
N-H (Å)	0.86	0.86
H···O (Å)	2.06	2.05
N···O (Å)	2.909(8)	2.896(16)
N-H···O (º)	168	166
	N13-H13N···O24	
N-H (Å)	0.86	0.86
H···O (Å)	2.17	2.14
N···O (Å)	3.014(7)	2.977(18)
N-H···O (º)	167	166
	N23-H23N···O12 (intra)	
N-H (Å)	0.86	0.86
H···O (Å)	2.07	2.06
N···O (Å)	2.907(8)	2.908(17)
N-H···O (º)	165	167
	N14-H14N···O23	
N-H (Å)	0.86	0.86
H···O (Å)	2.18	2.14
N···O (Å)	3.023(8)	2.980(18)
N-H···O (º)	167	165
	N24-H24N···O14^{ii} (intra)	
N-H (Å)	0.86	0.86
H···O (Å)	2.07	2.05
N···O (Å)	2.908(7)	2.890(18)
N-H···O (º)	165	165

symmetry codes: (i): 1-*x*, *y*, -*z*; (ii): -*x*, *y*, 1-*z* (*C*2)

27 Possible H-bond patterns in ferrocene bis-amides

The results of conformational search for **2b** were rationalized by analyzing possible ways to get as many amide H-bonds as possible. The scheme below shows all possible combinations of H-bonding between CO and NH groups in **2b**. The most stable conformers found by computational search (**2b-I**, **2b-II**, **2b-III**) exhibit exactly the H-bond patterns shown below in the top two rows. Actually, one O…H distance in **2b-II** is too big (2.95 A) to be considered as an H-bond, but there is another conformer (**2b-IV**, not shown) with the same H-bond pattern as in **2b-II** and with all O…H distances below 2 Å (yet, its energy is 3 kcal/mol higher than **2b-II**). No other conformers have any of the patterns below. The patterns in the bottom two rows are impossible to realize geometrically. This demonstrates that hydrogen bonding is a useful lead in the conformational search of small (pseudo)peptide molecules and also confirms that the present search was exhaustive.



28 Figures, additional information

28.1 Figure 1 concentrations

a)

2b 3.67 mM

1b 10.131 mM

b)

2b 10.45 mM

1b 11.444 mM

c)

2b c = 6.85 mM

1b c = 8.18 mM

d)

2b 4.02017 mM

1b 4.4914 mM

28.2 Figure 4 a)

c ≈ 3 mM

Tfa equivalents	Tfa volume fraction/%
0	0
1	0.028977108
2	0.057110223
3	0.084435688
4	0.110987791
5	0.136798906
6	0.161899622
7	0.186318871
8	0.210084034
9	0.233221042
10	0.255754476
11	0.27770765
12	0.299102692
13	0.31996062
14	0.34030141
15	0.360144058
16	0.379506641
17	0.398406375
18	0.416859657

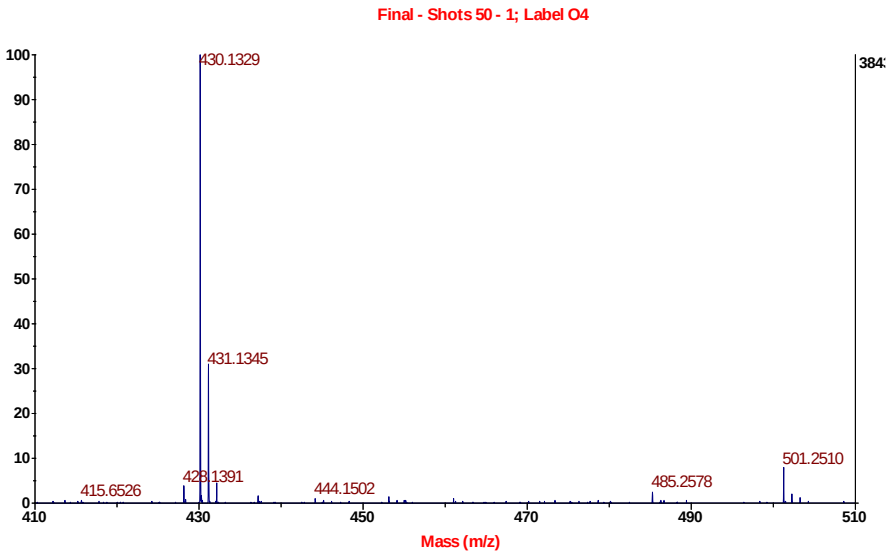
28.3 Figure 4 b)

c≈ 0.2 mM

Tfa equivalents	Tfa volume fraction/%
0	0
1	0.011012003
2	0.021829295
3	0.032456994
4	0.042900043
5	0.053163211
6	0.063251107
7	0.073168182
8	0.08291874
9	0.092506938
10	0.101936799
11	0.111212213
12	0.120336943
13	0.129314632
14	0.138148806
15	0.146842878
103	0.199600798
362	0.497512438

29 High resolution mass spectra

29.1 1b

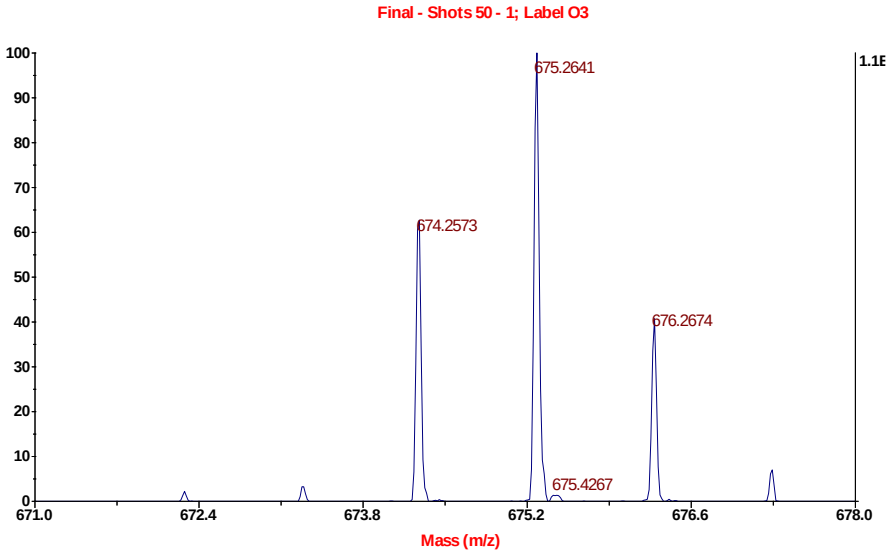


$C_{24}H_{26}FeN_2O_2$+

Calculated mass: 430.1343701892

Measured mass: 430.1329

29.2 2b

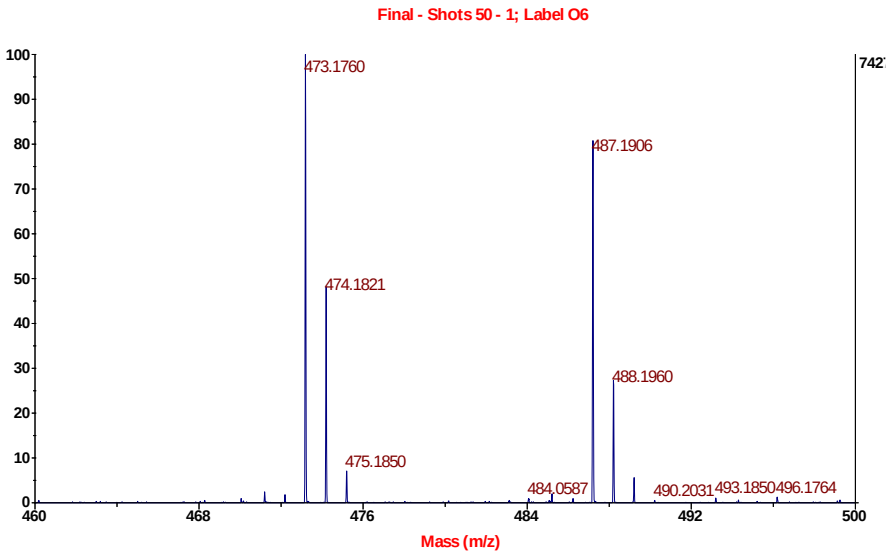


$C_{38}H_{42}FeN_4O_4$+

Calculated mass: 674.2555479574

Measured mass: 674.2573

29.3 1n

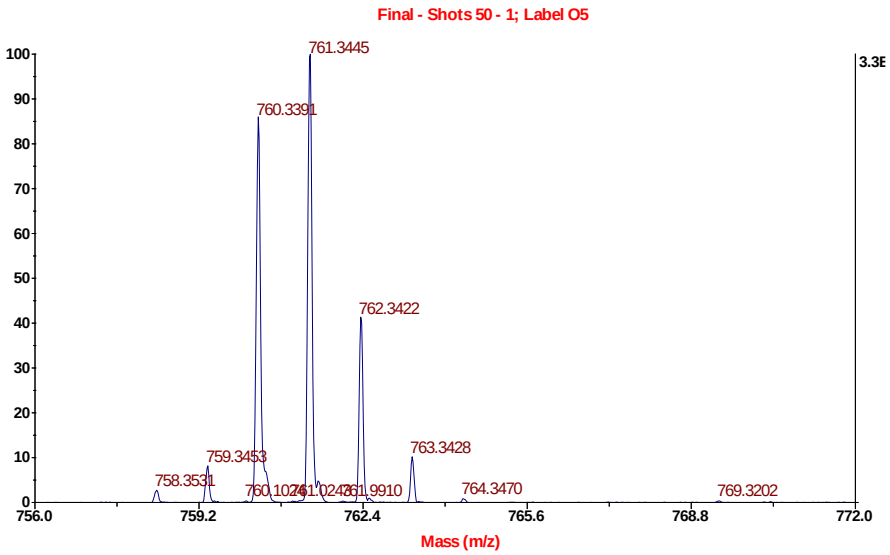


$C_{26}H_{31}FeN_3O_2$+

Calculated mass: 473.1765693549

Measured mass: 473.1760

29.4 2n

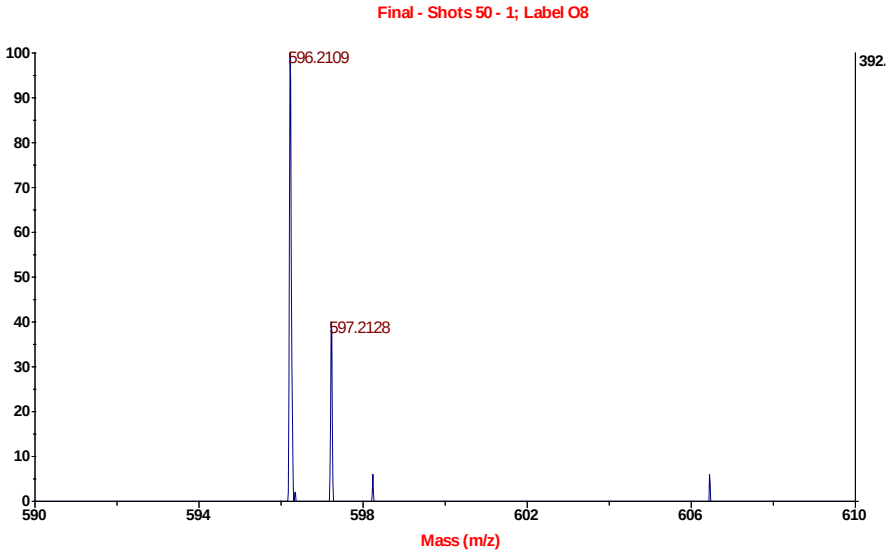


$C_{42}H_{52}FeN_6O_4+$

Calculated mass: 760.3399462888

Measured mass: 760.3391

29.5 1t

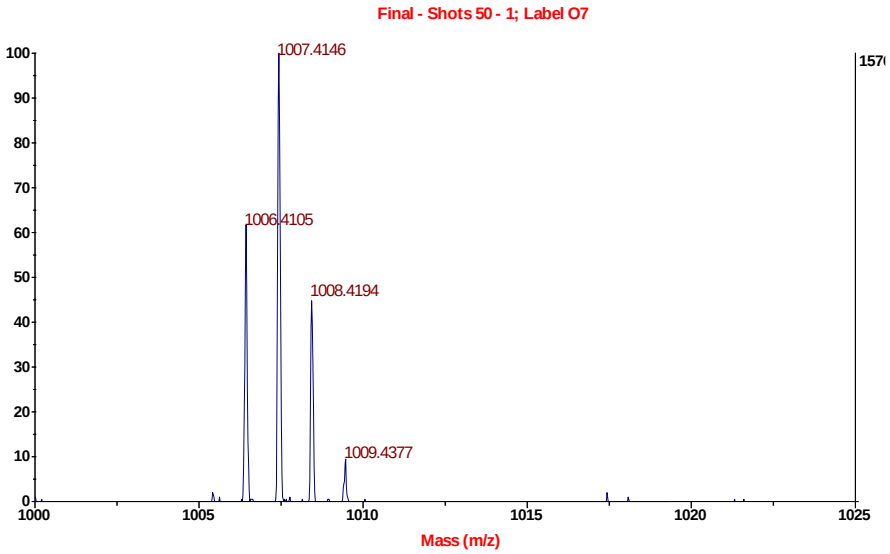


$C_{37}H_{36}FeN_2O_2$+

Calculated mass: 596.2126205102

Measured mass: 596.2109

29.6 2t



$C_{64}H_{62}FeN_4O_4$+

Calculated mass:1006.4120485994

Measured mass: 1006.4105

30 References

1 S. I. Kirin, H. B. Kraatz and N. Metzler-Nolte, *Chem. Soc. Rev.*, 2006, **35**, 348–354.

2 Z. Kokan, Z. Glasovac, M. Majerić Elenkov, M. Gredičak, I. Jerić and S. I. Kirin, *Organometallics*, 2014, **33**, 4005–4015.

3 S. Opačak, Z. Kokan, Z. Glasovac, B. Perić and S. I. Kirin, *Eur. J. Org. Chem.*, 2019, **2019**, 2115–2128.

4 Z. Kokan and S. I. Kirin, *RSC Adv.*, 2012, **2**, 5729–5737.

5 M. Pernar, Z. Kokan, J. Kralj, Z. Glasovac, L. M. Tumir, I. Piantanida, D. Eljuga, I. Turel, A. Brozovic and S. I. Kirin, *Bioorg. Chem.*, 2019, **87**, 432–446.

6 Z. Kokan, B. Perić, M. Vazdar, Ž. Marinić, D. Vikić-Topić, E. Meštrović and S. I. Kirin, *Chem. Commun.*, 2017, **53**, 1945–1948.