Supporting Information

Luminescent, Redox-active Diphenothiazine Dumbbells Expanded by Conjugated Arenes and Heteroarenes

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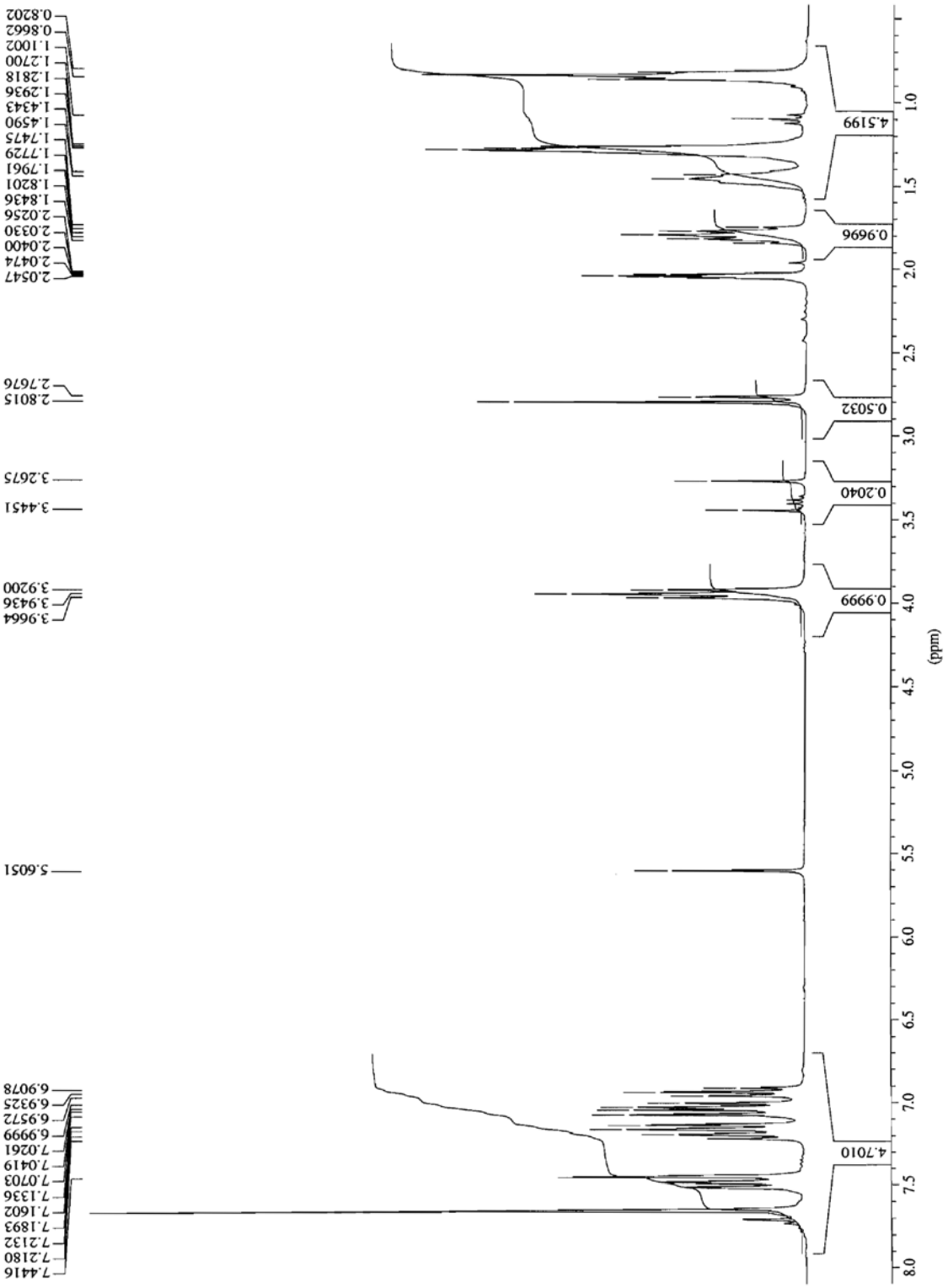
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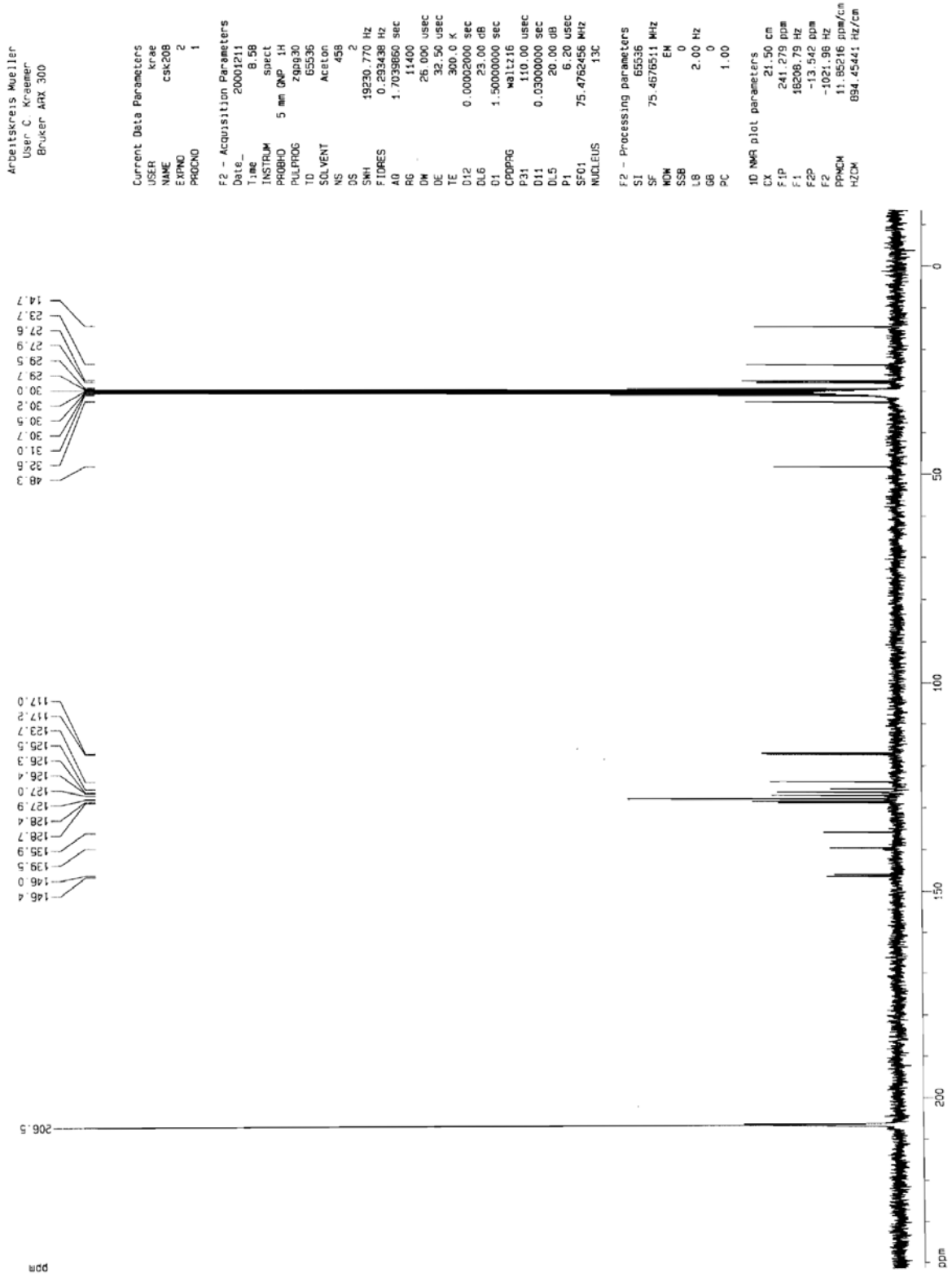
1. ^{1}H and ^{13}C NMR spectra of compounds 2g-o, 7, and 9

Compound 2g

^{1}H NMR (300 MHz, d^{6}-acetone)

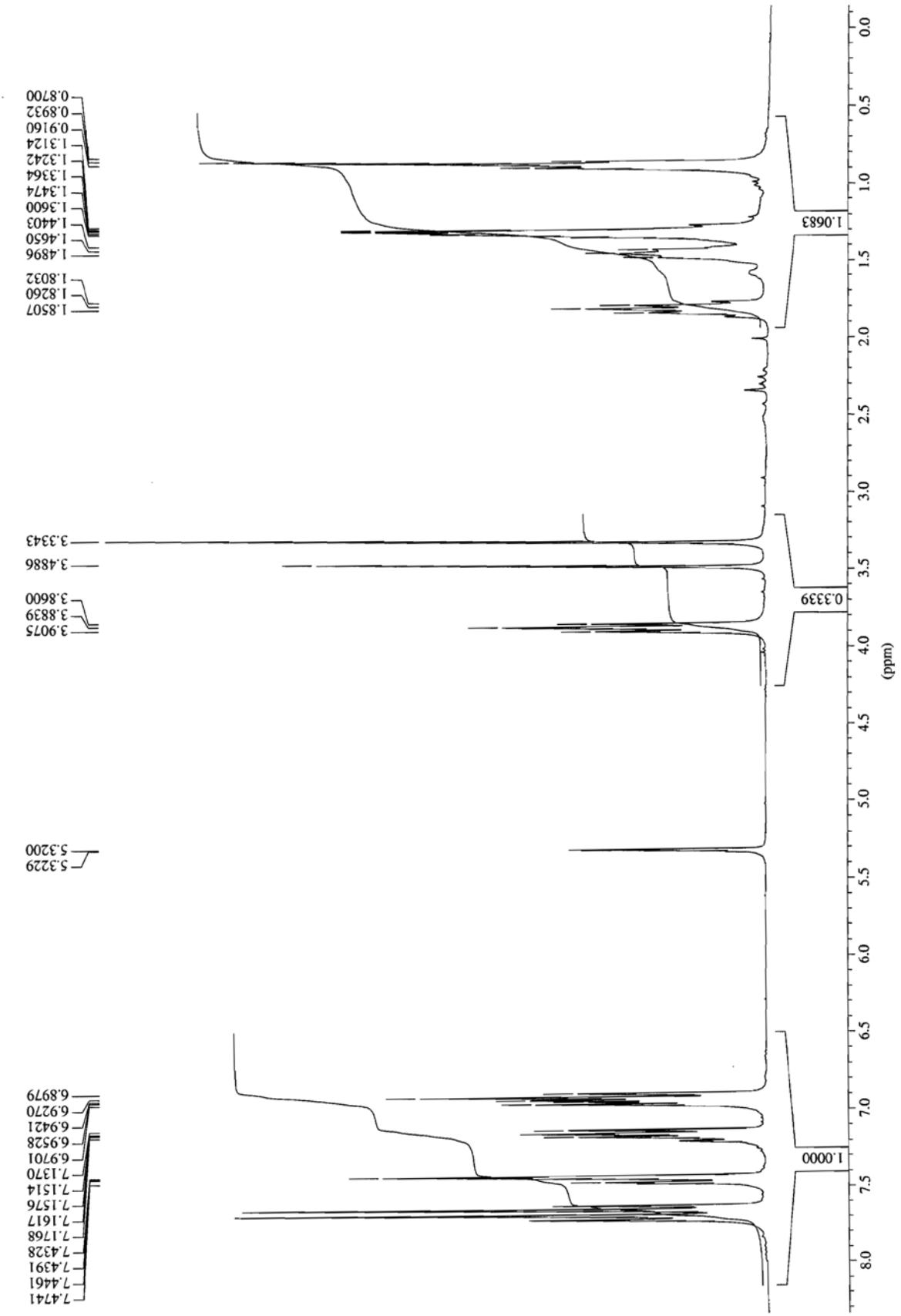


^{13}C NMR (75 MHz, d^6-acetone)

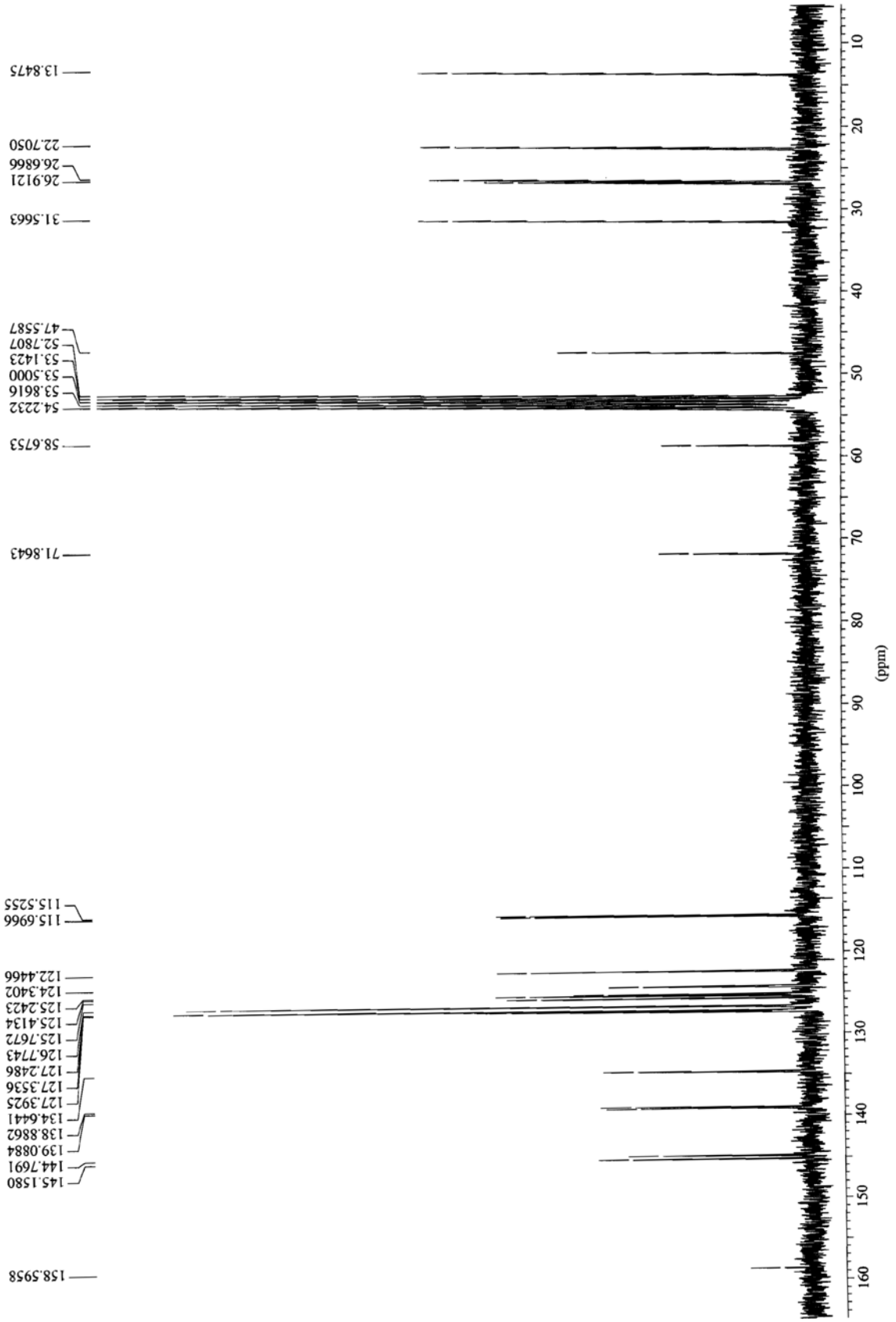


Compound 2h

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

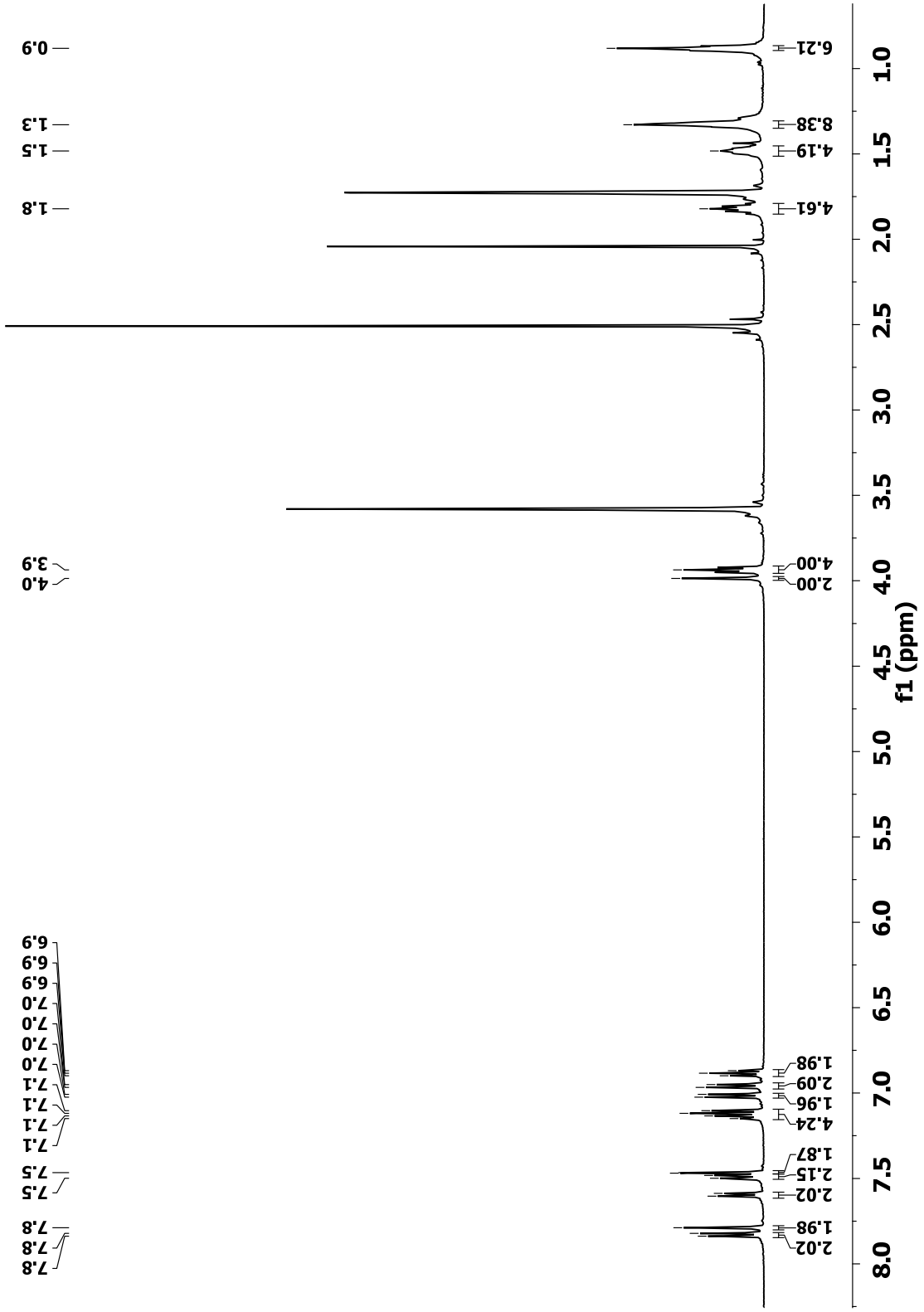


^{13}C NMR (75 MHz, CD_2Cl_2)

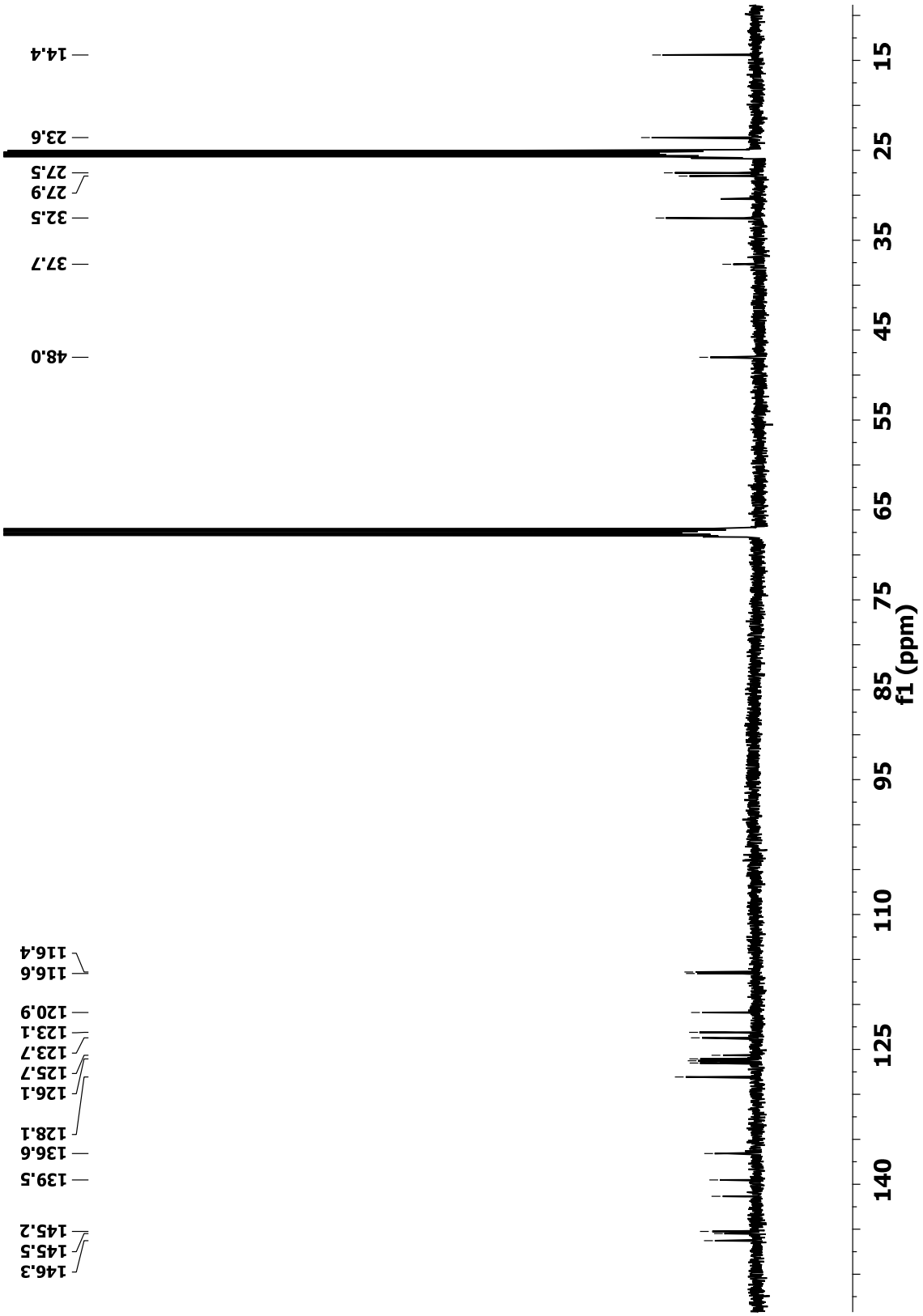


Compound 2i

^{1}H NMR (500 MHz, d^{8}-THF)

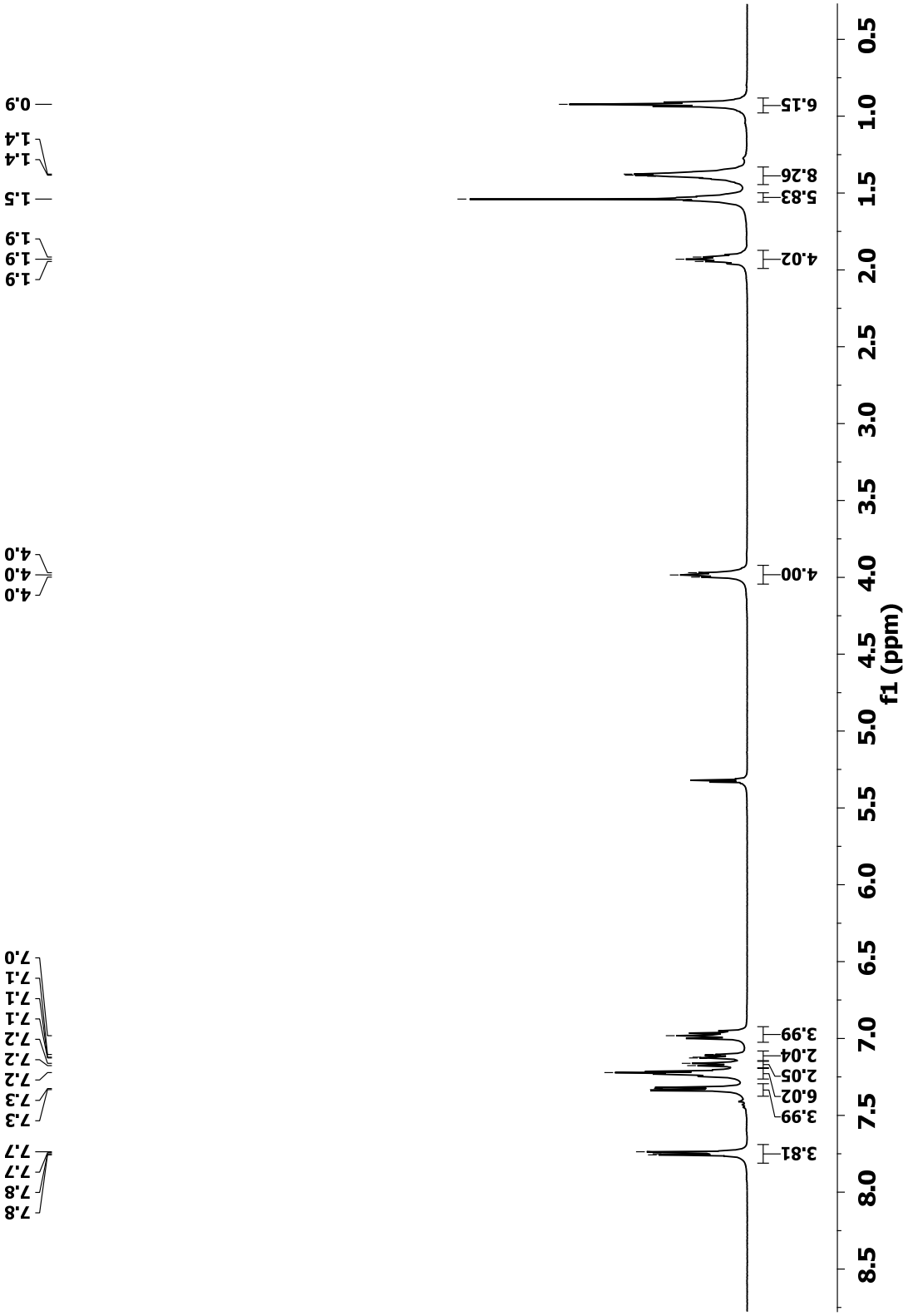


^{13}C NMR (125 MHz, d^{8}-THF)

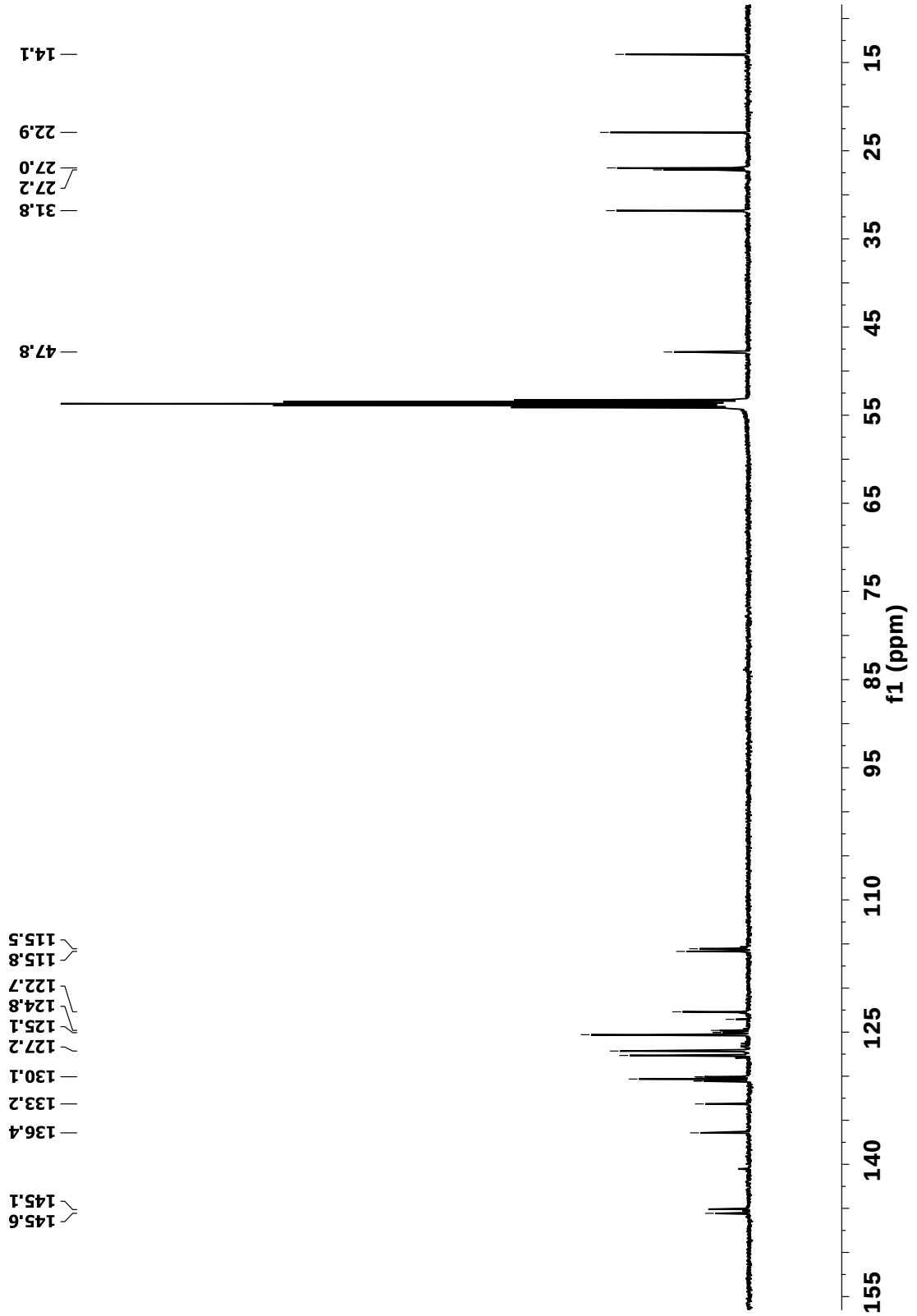


Compound 2j

^{1}H NMR (500 MHz, CD_2Cl_2)

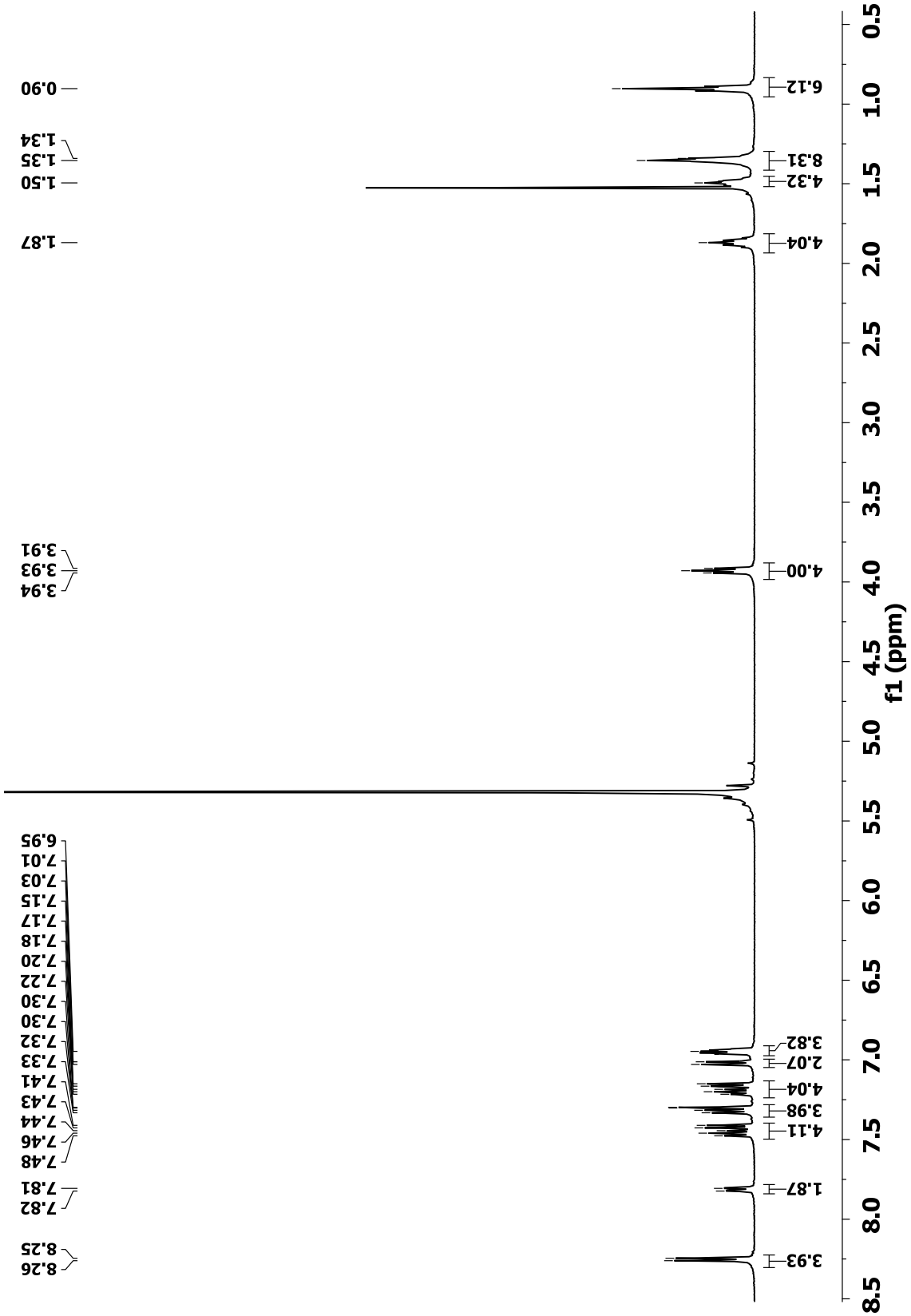


^{13}C NMR (125 MHz, CD_2Cl_2)

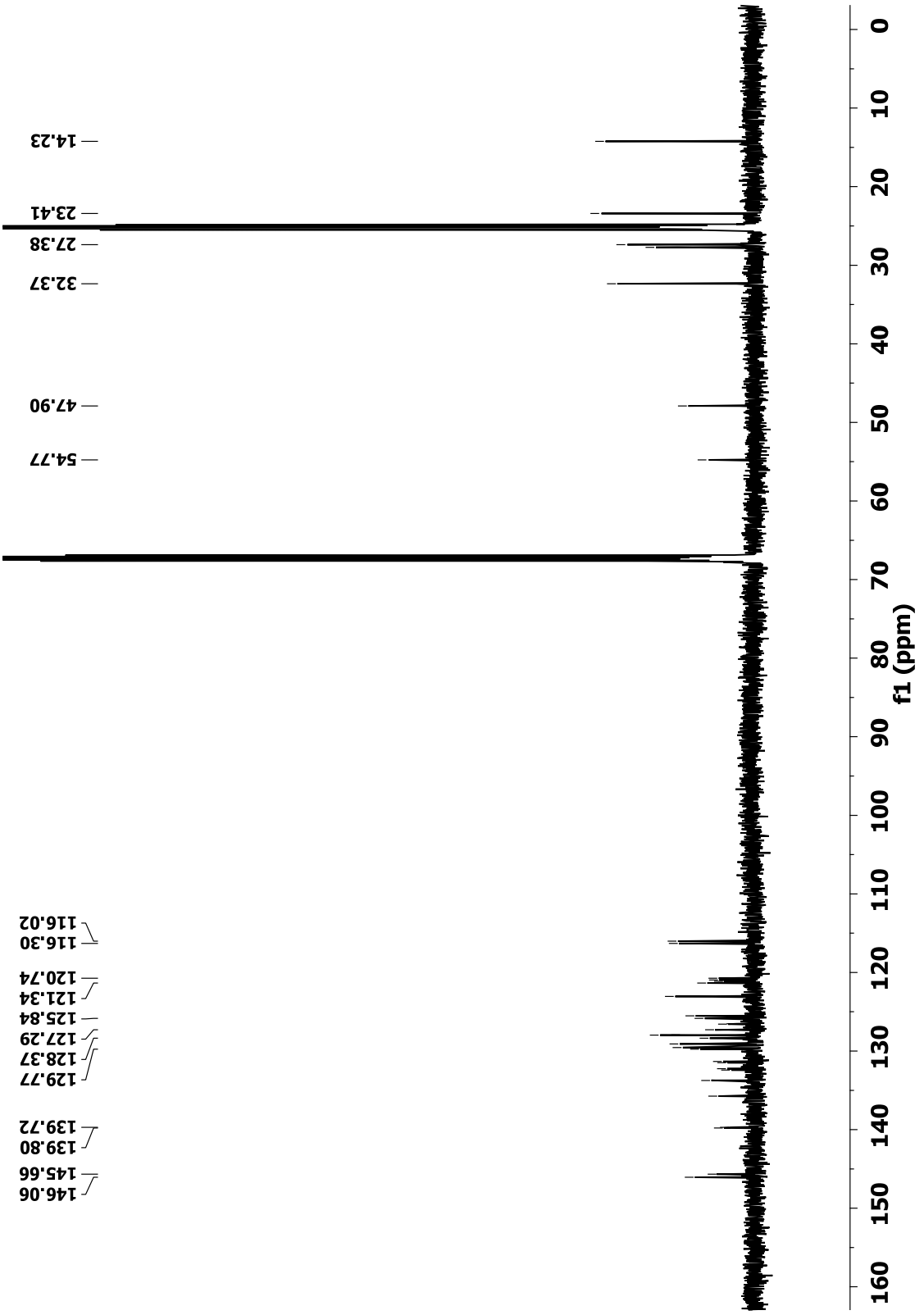


Compound 2k

^{1}H NMR (500 MHz, CD_2Cl_2)

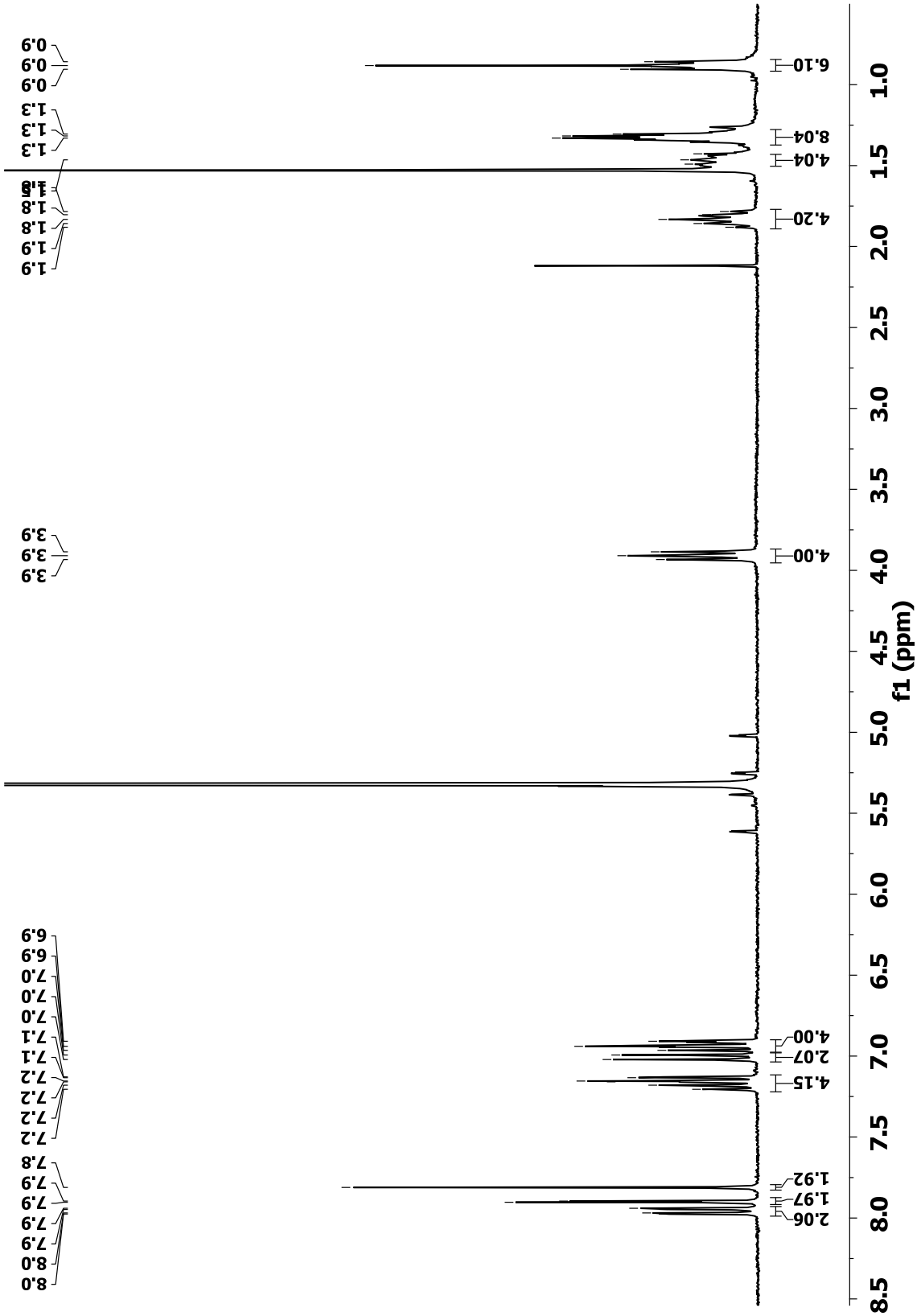


^{13}C NMR (125 MHz, CD_2Cl_2)

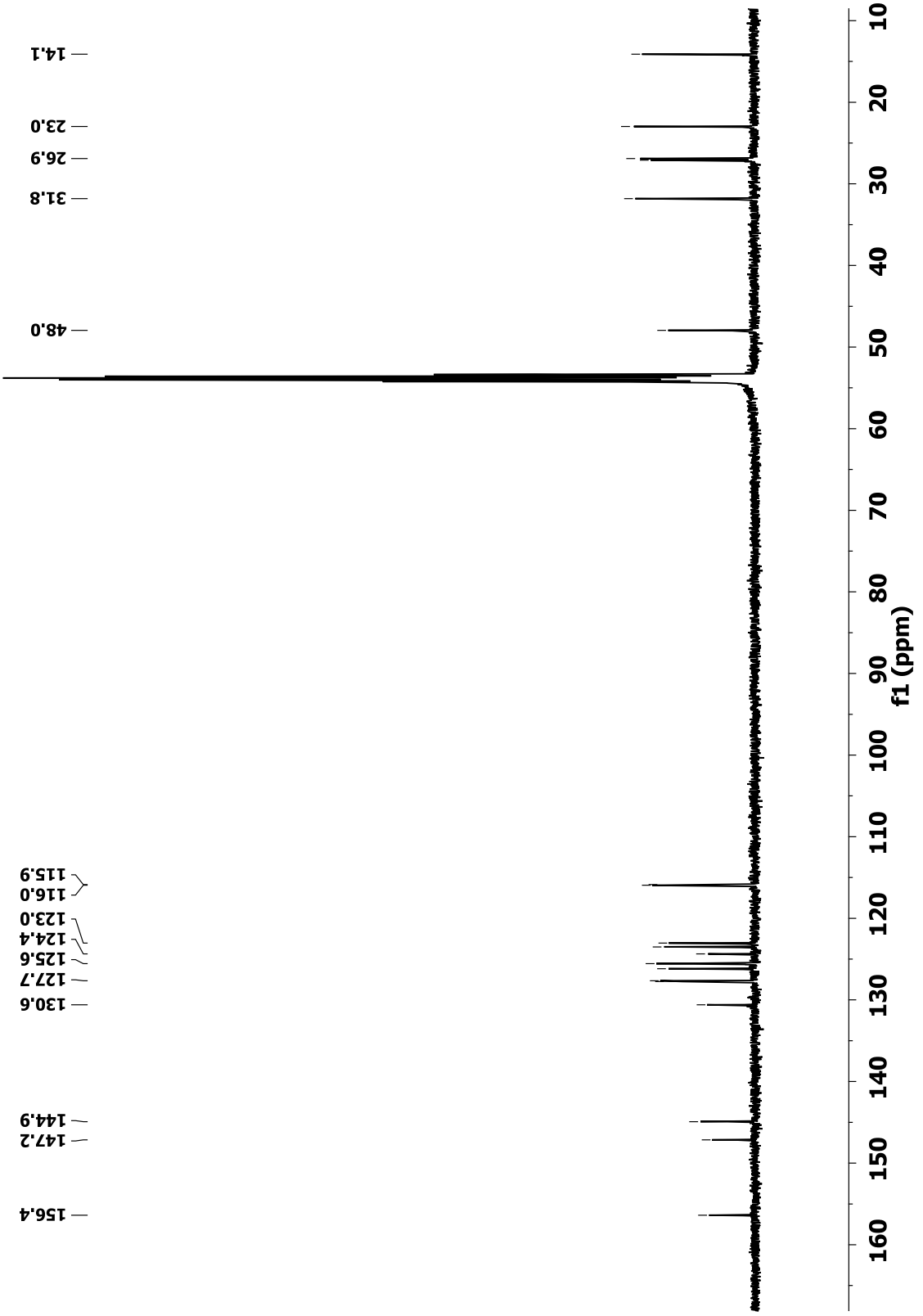


Compound 2l

^{1}H NMR (500 MHz, CD_2Cl_2)

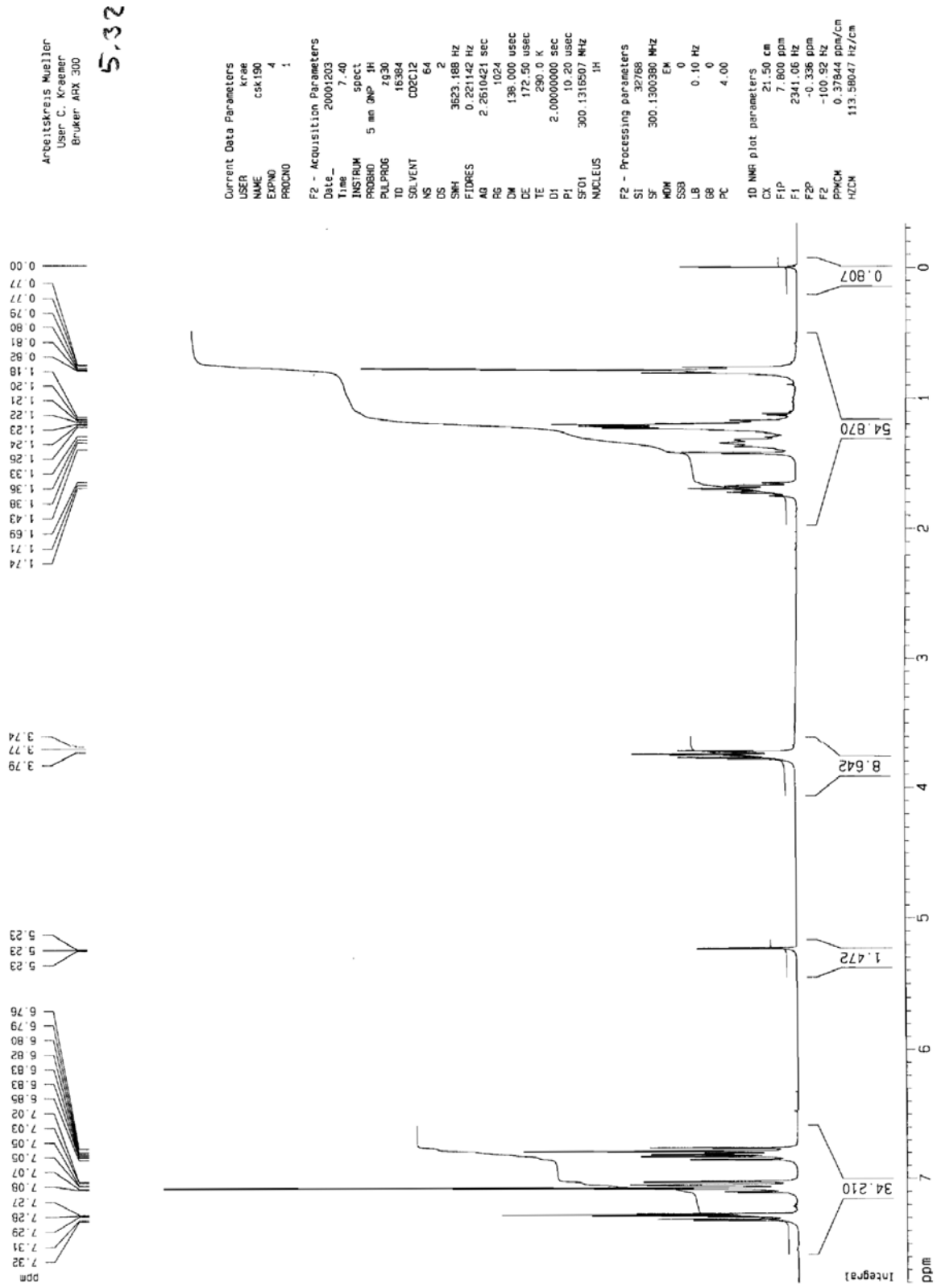


^{13}C NMR (125 MHz, CD_2Cl_2)

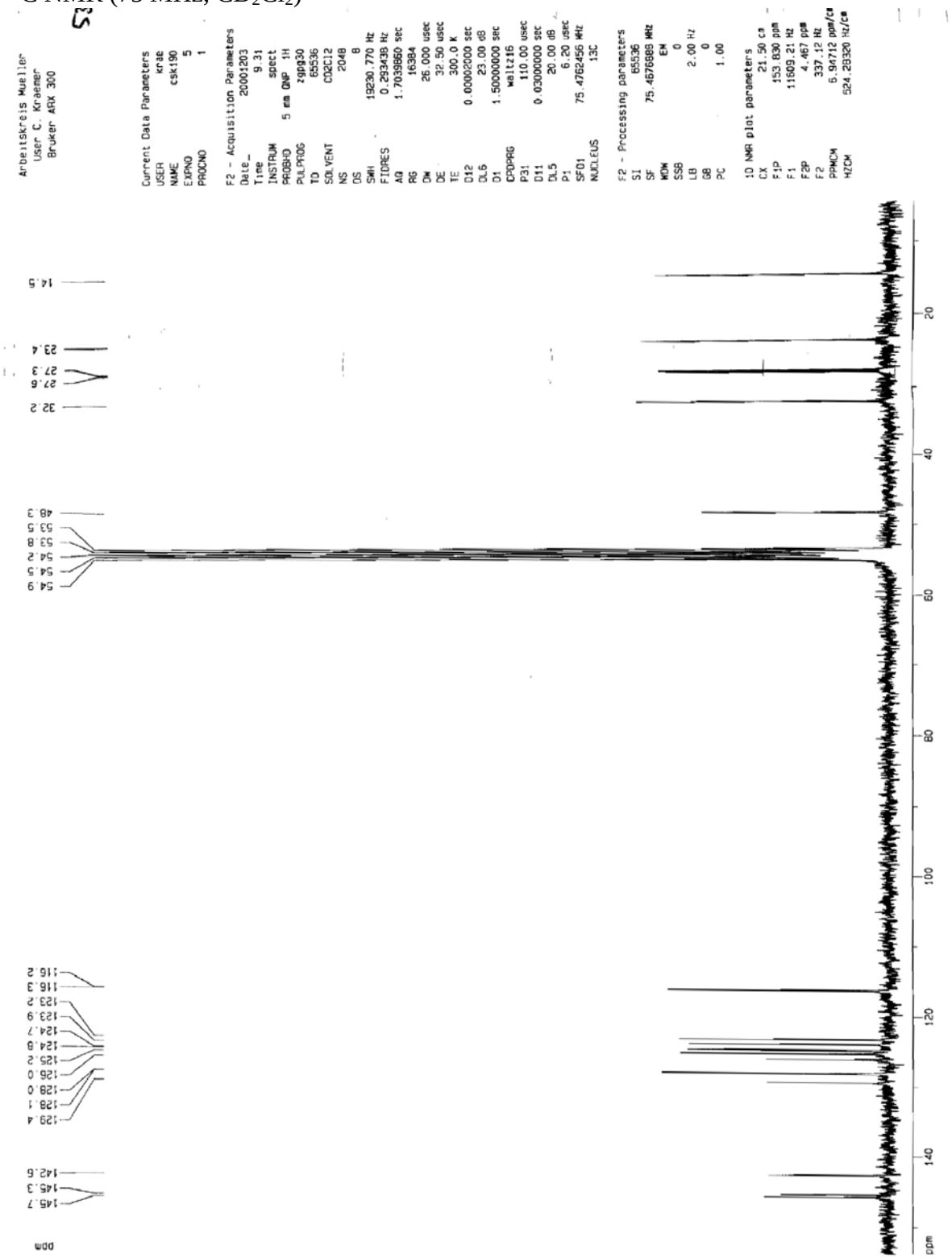


Compound 2m

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

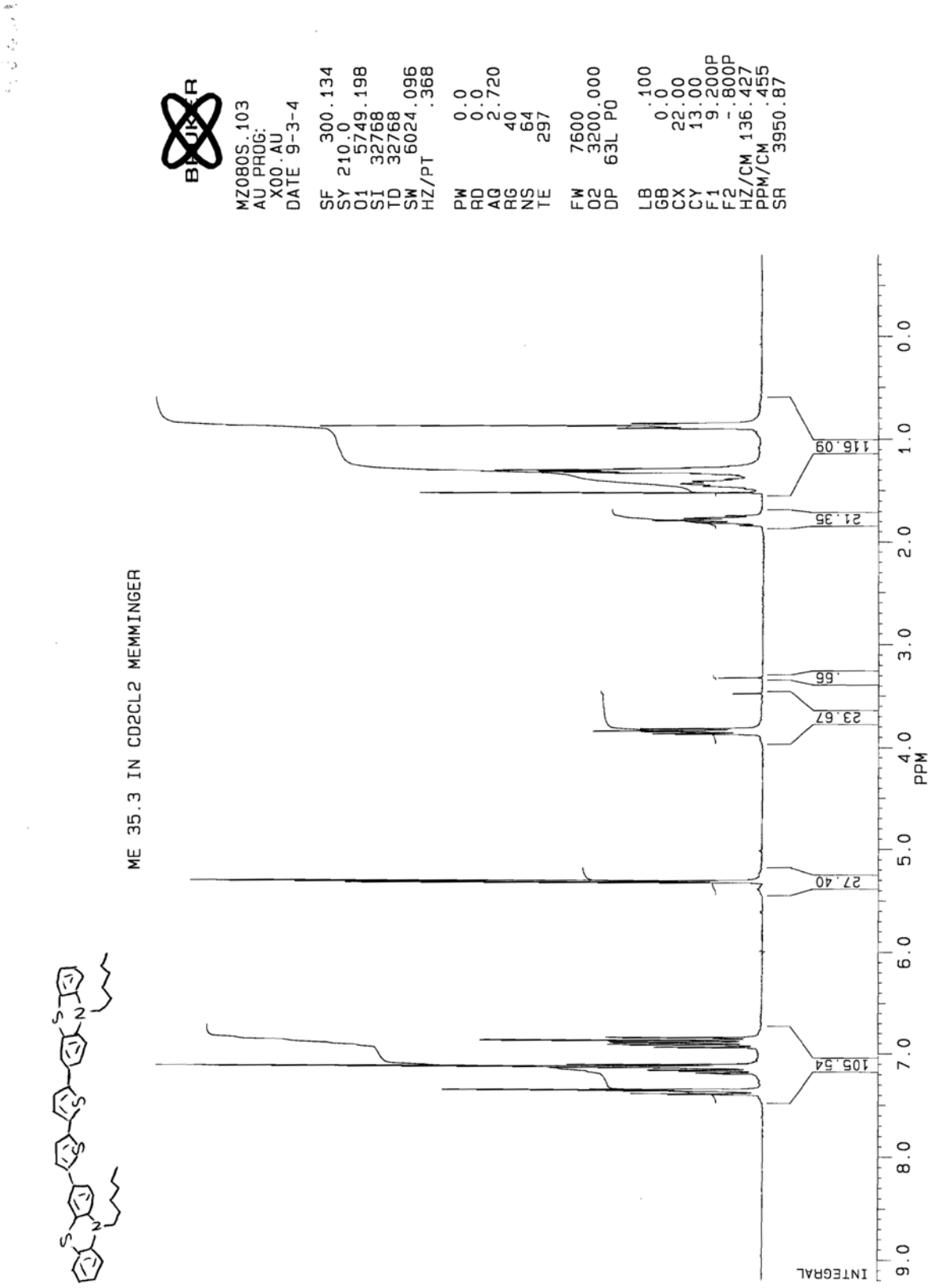


^{13}C NMR (75 MHz, CD_2Cl_2)

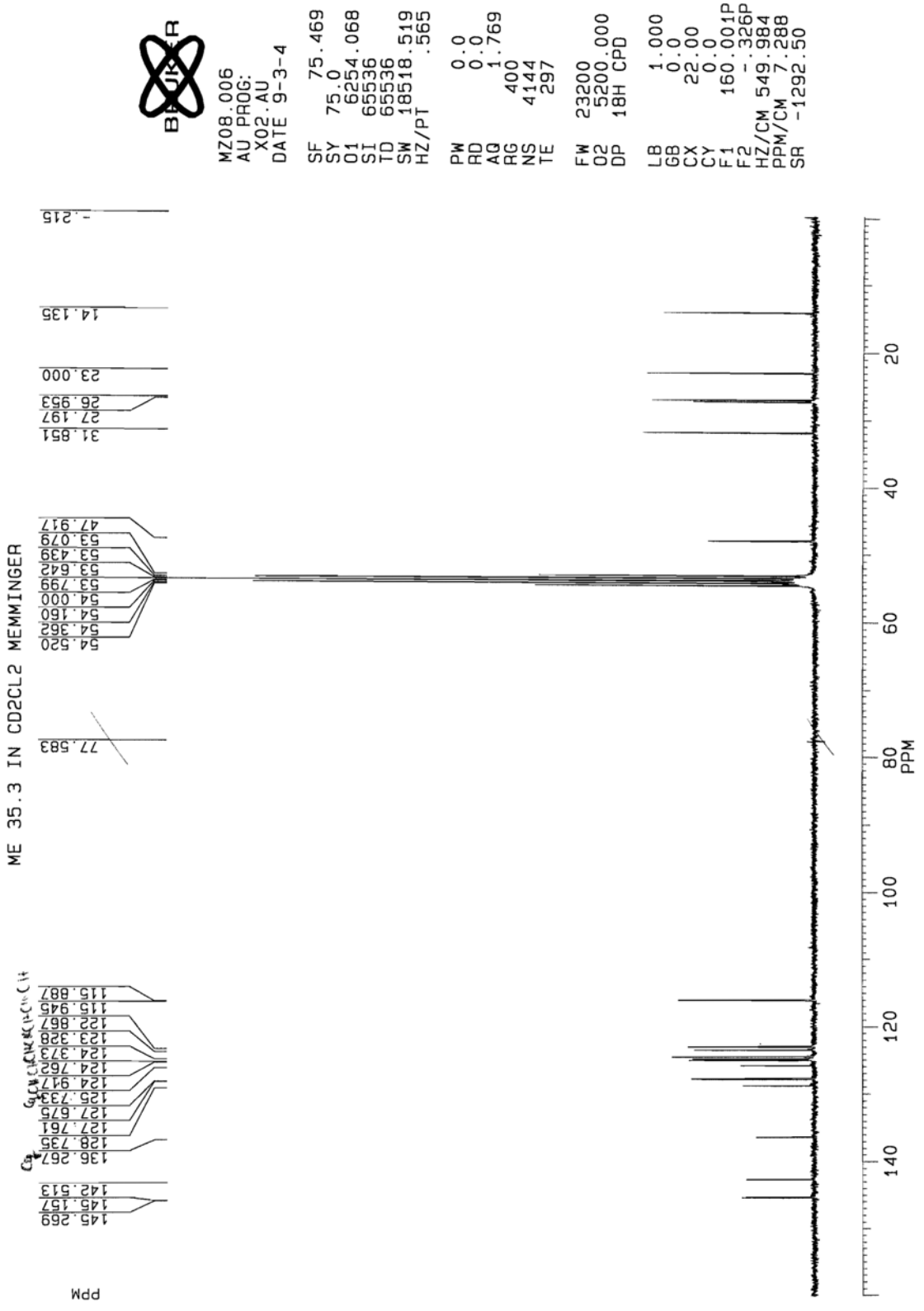


Compound 2n

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

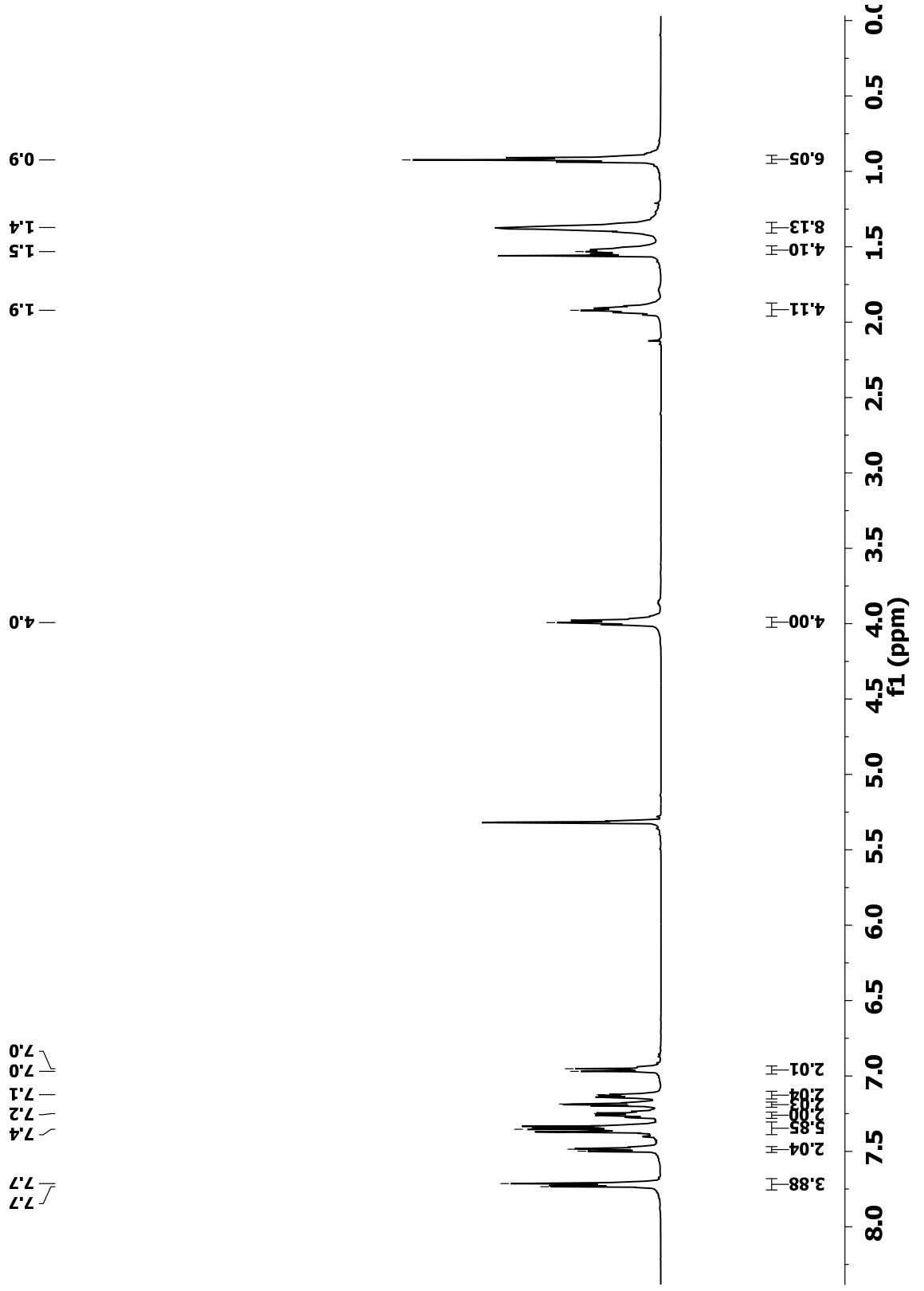


^{13}C NMR (75 MHz, CD_2Cl_2)

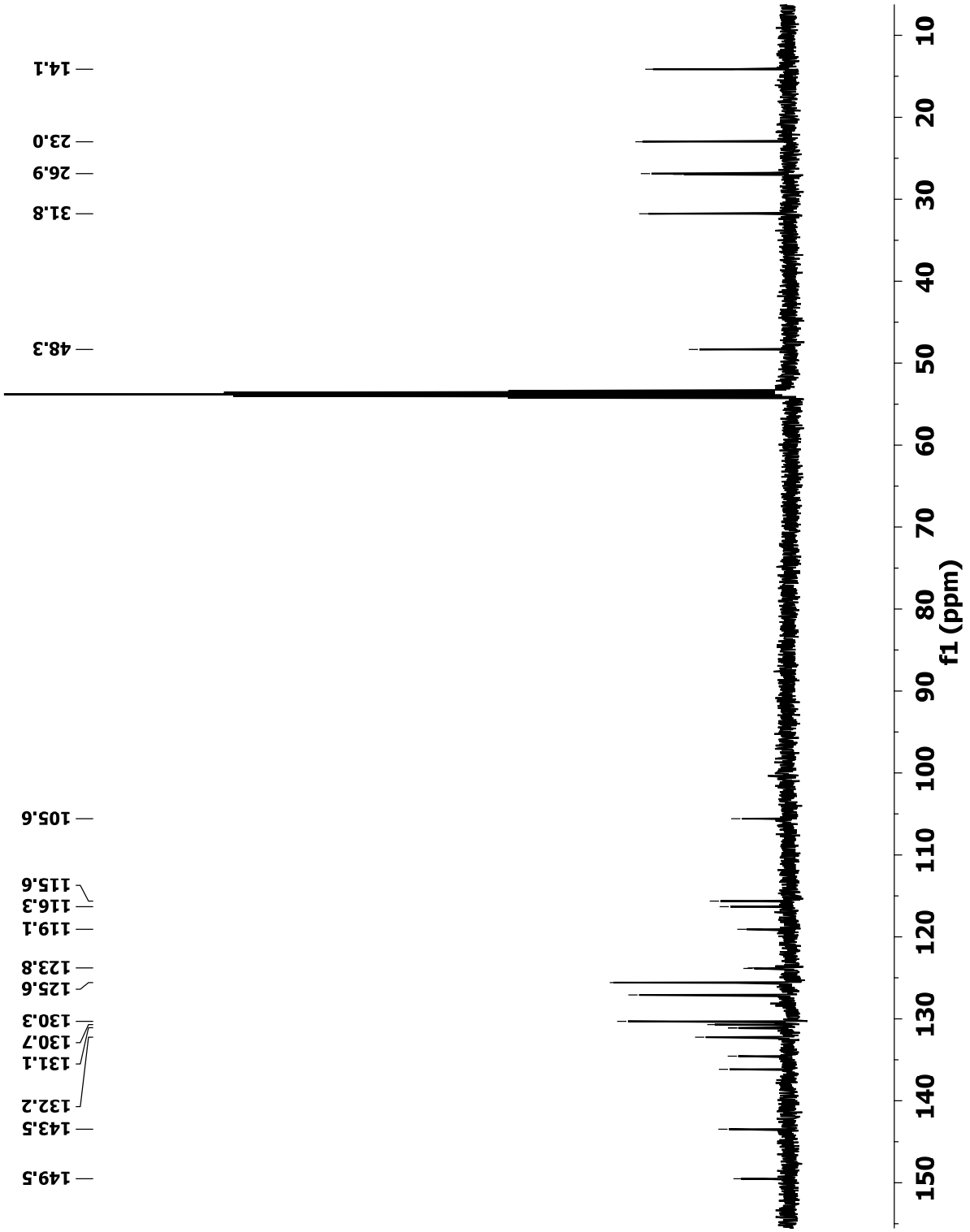


Compound 2o

^{1}H NMR (500 MHz, CD_2Cl_2)

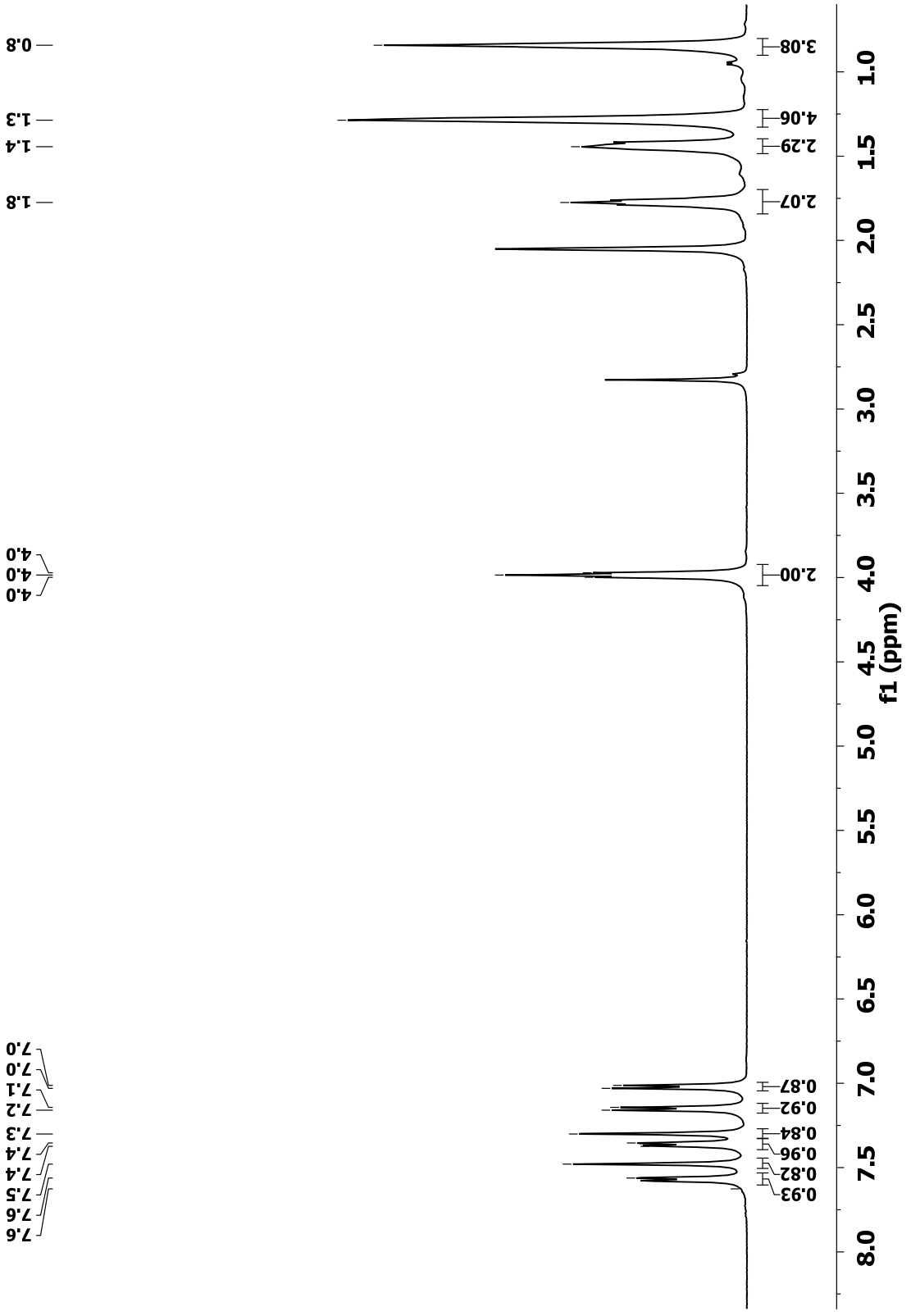


^{13}C NMR (125 MHz, CD_2Cl_2)

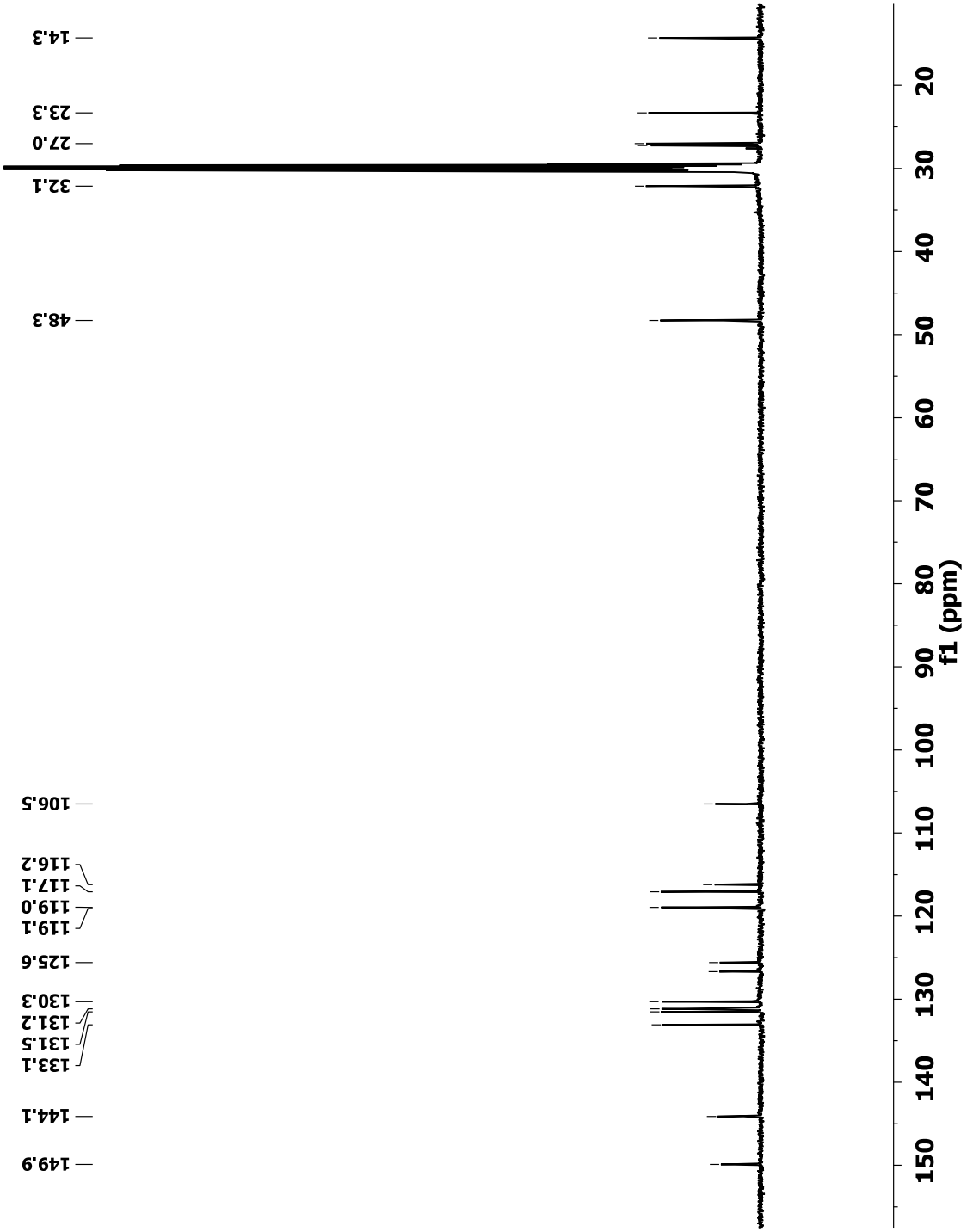


Compound 7

^{1}H NMR (500 MHz, acetone-d^{6})

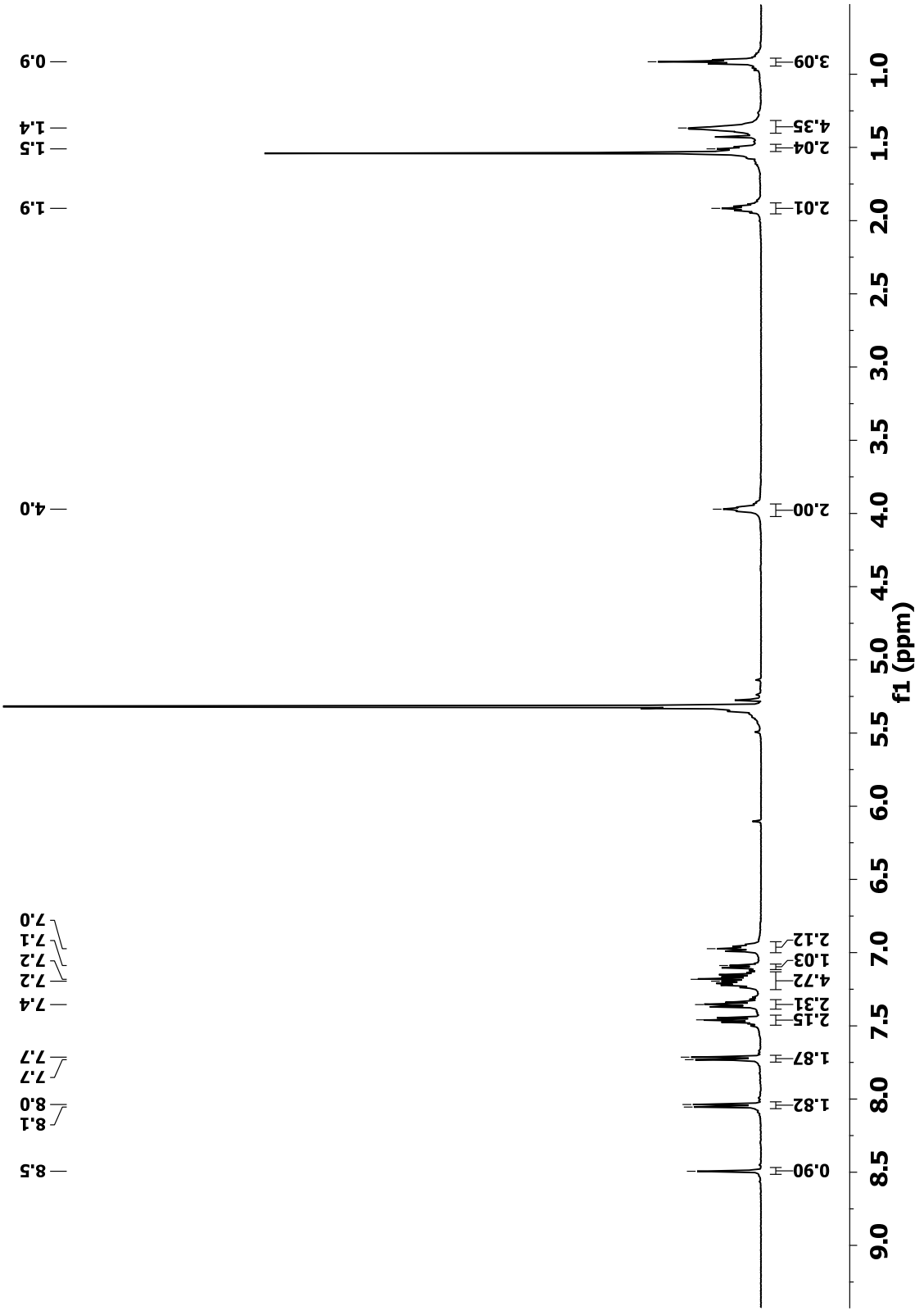


^{13}C NMR (125 MHz, acetone-d^{6})

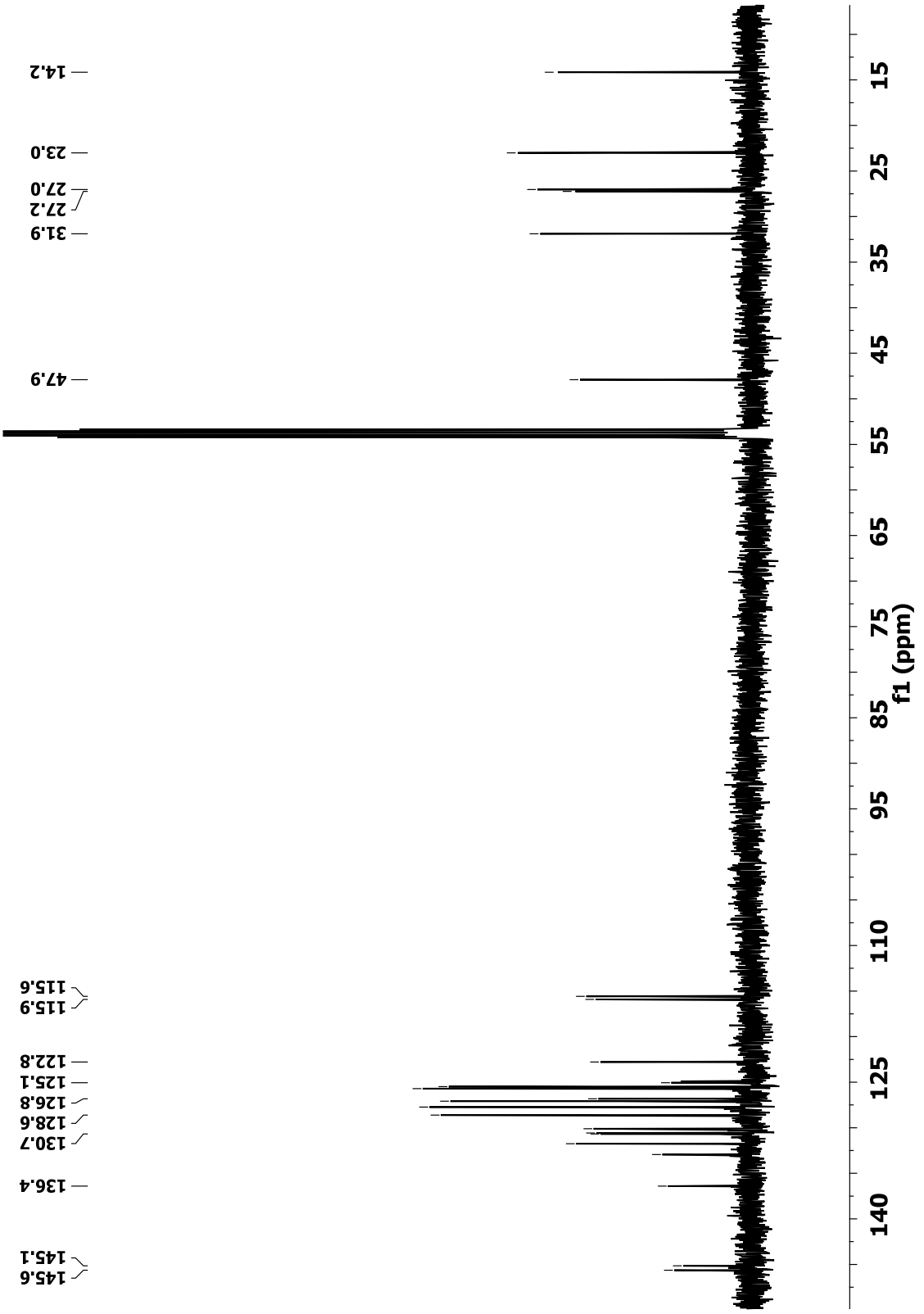


Compound 9

^{1}H NMR (500 MHz, CD_2Cl_2)

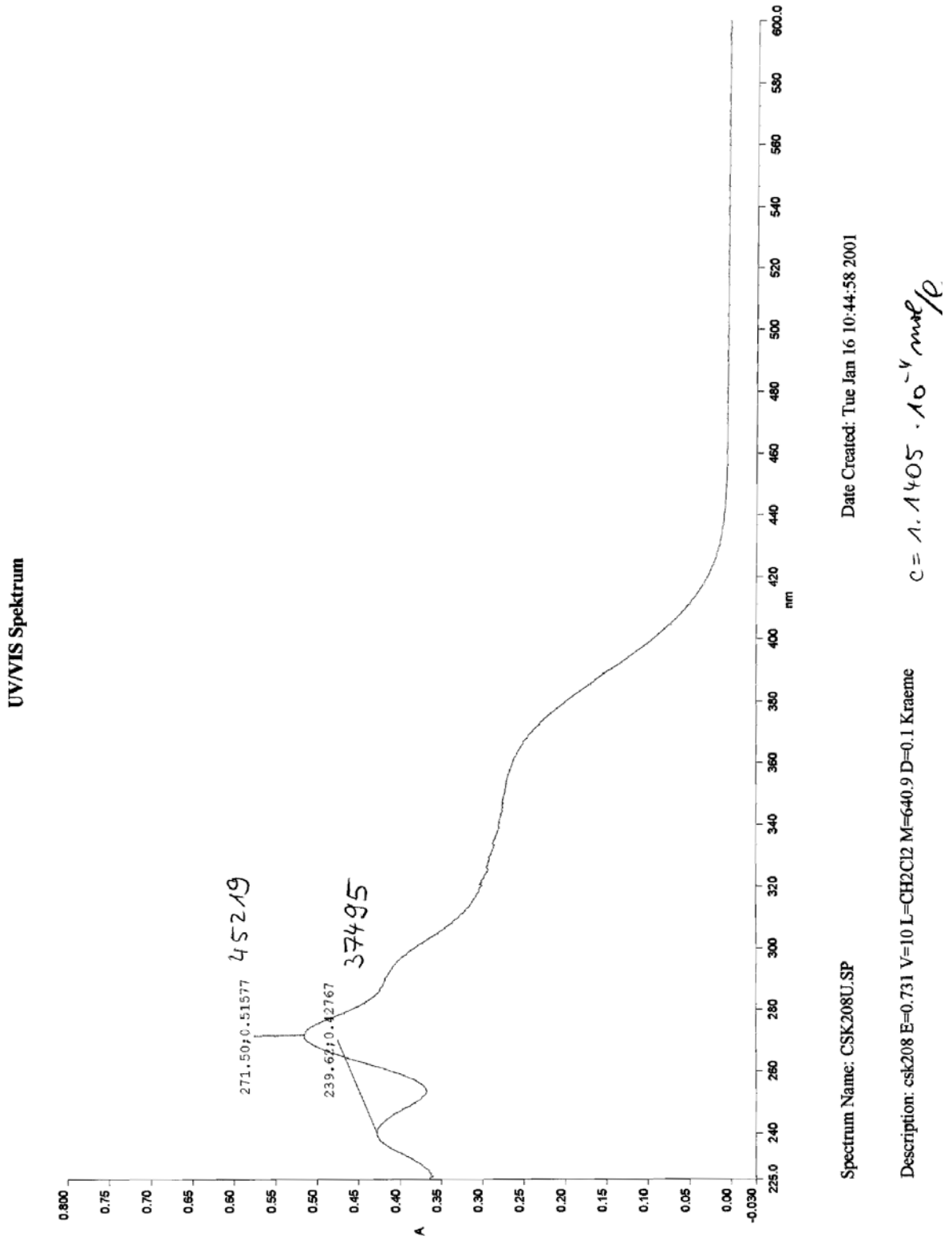


^{13}C NMR (125 MHz, CD_2Cl_2)

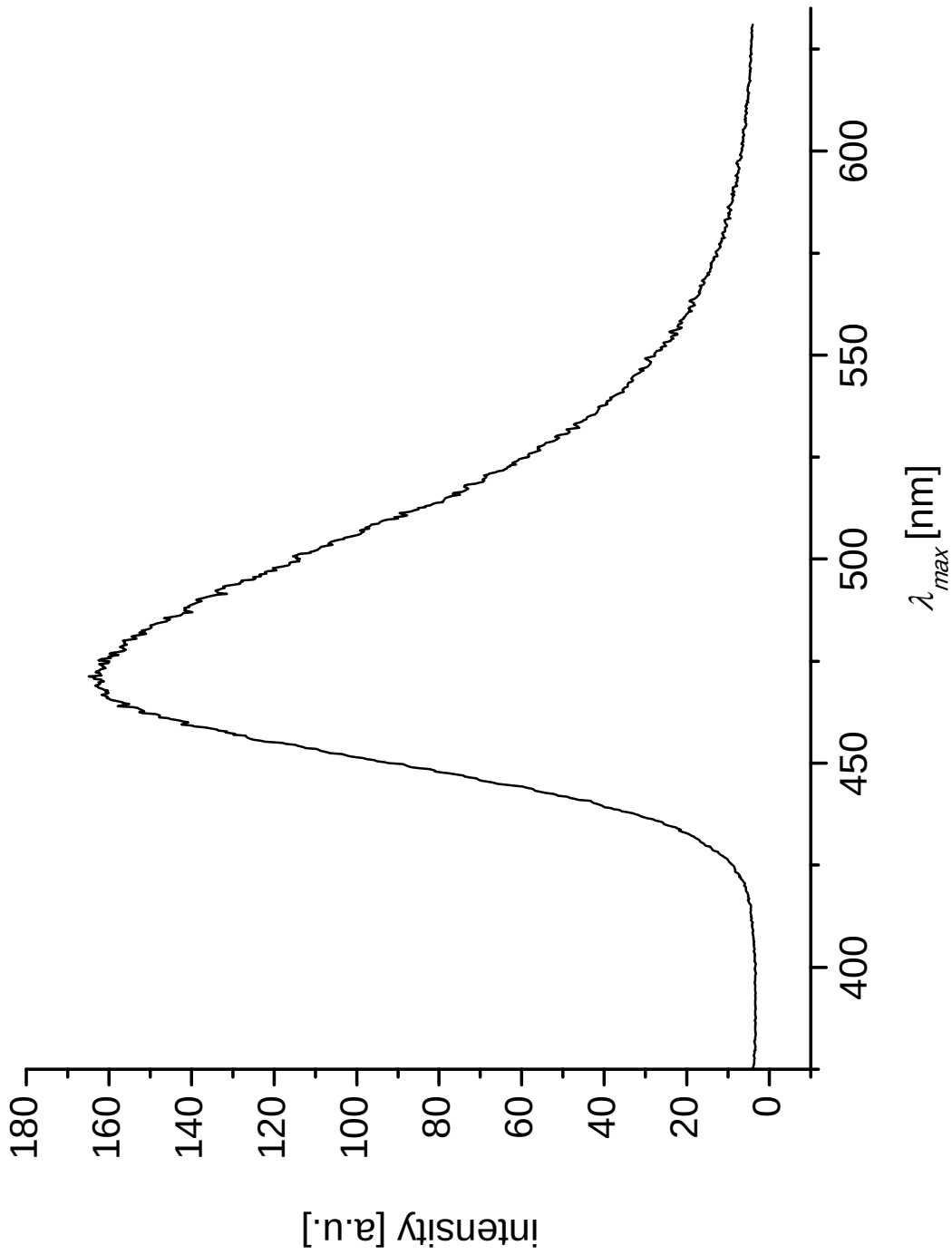


2. Selected UV/Vis and fluorescence spectra of compounds 2g-o, and 9

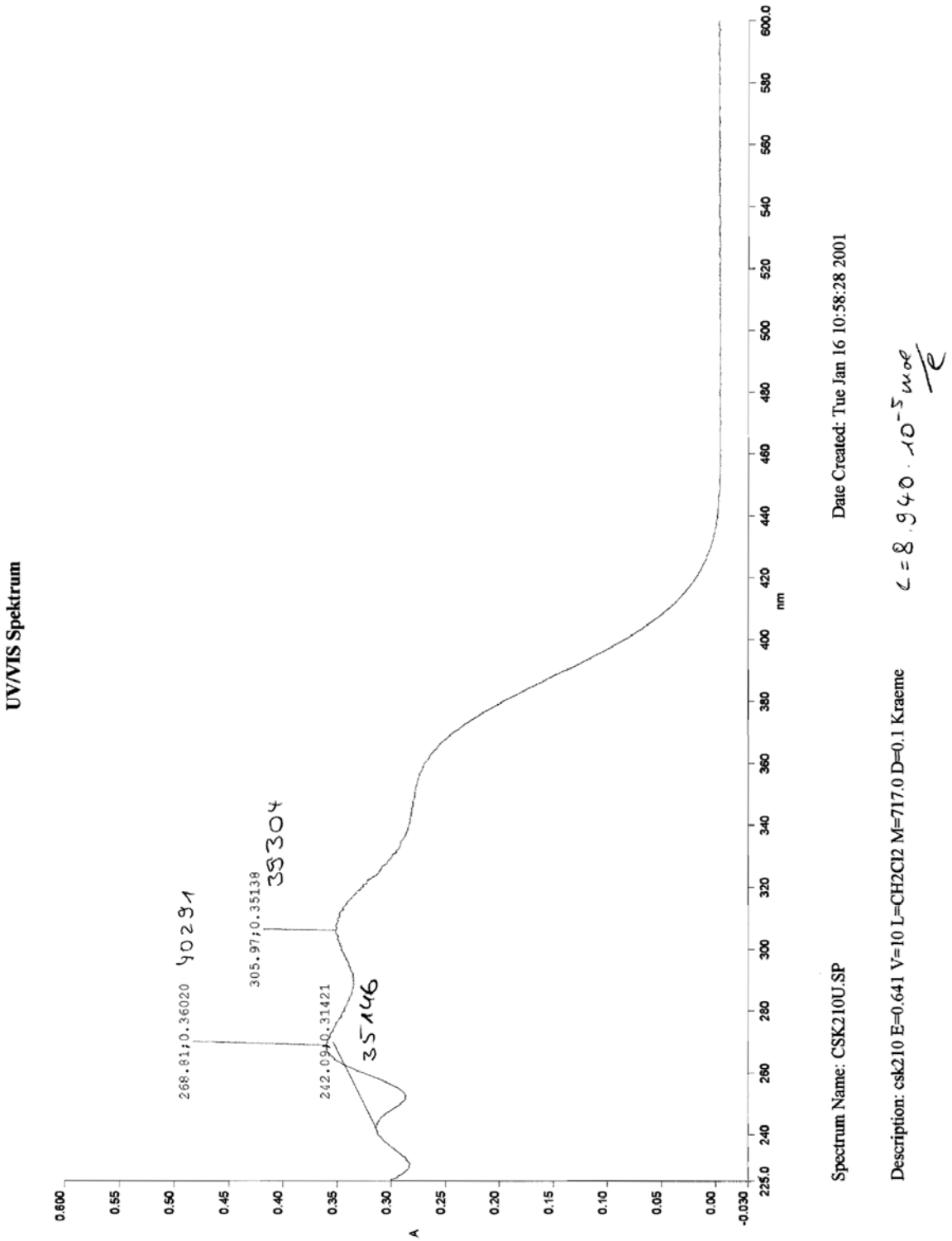
Compound 2g
(recorded in CH_2Cl_2, 20 °C)
Absorption



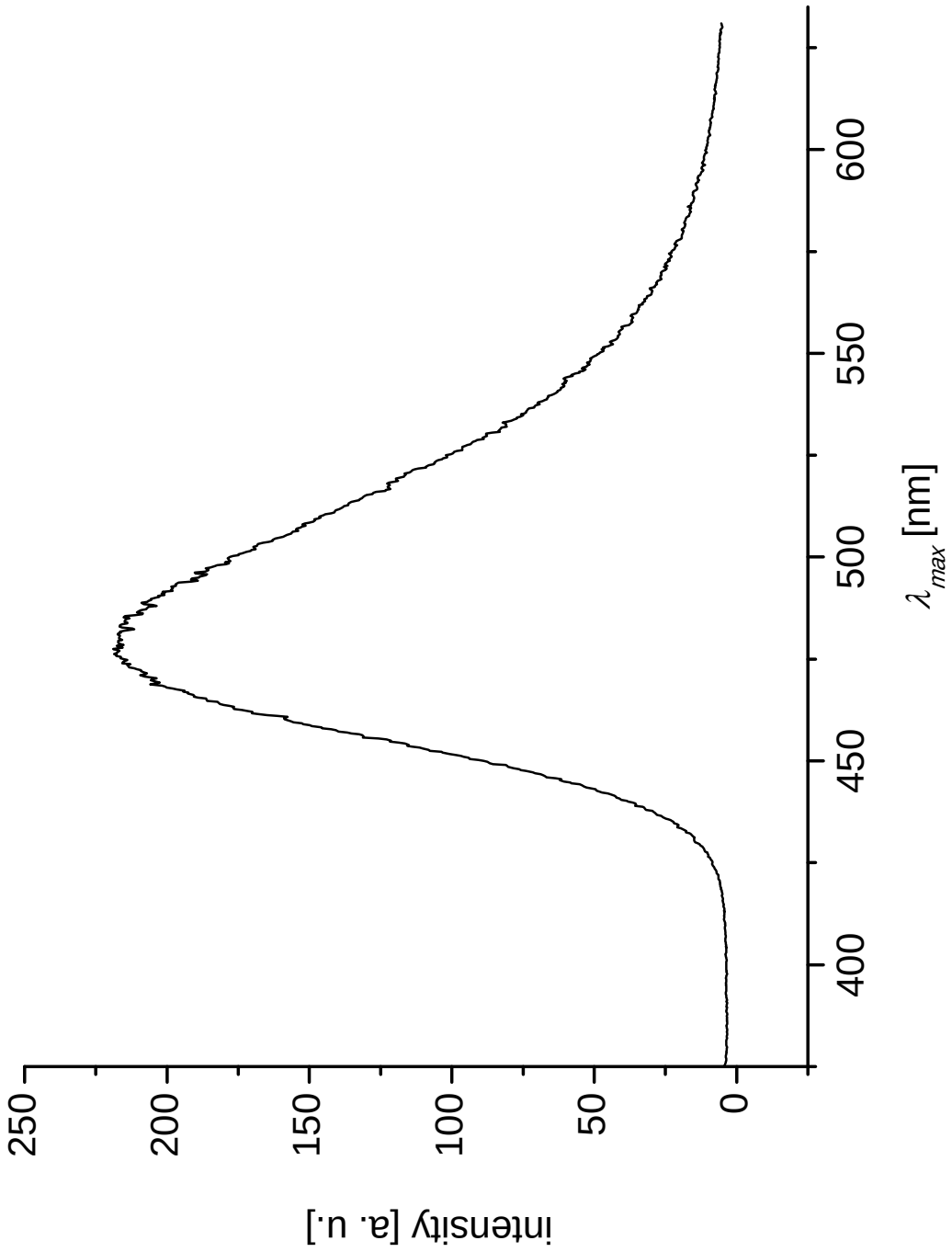
Emission


intensity [a.u.]
0
20
40
60
80
100
120
140
160
180
400
450
500
550
600
λ_{max} [nm]

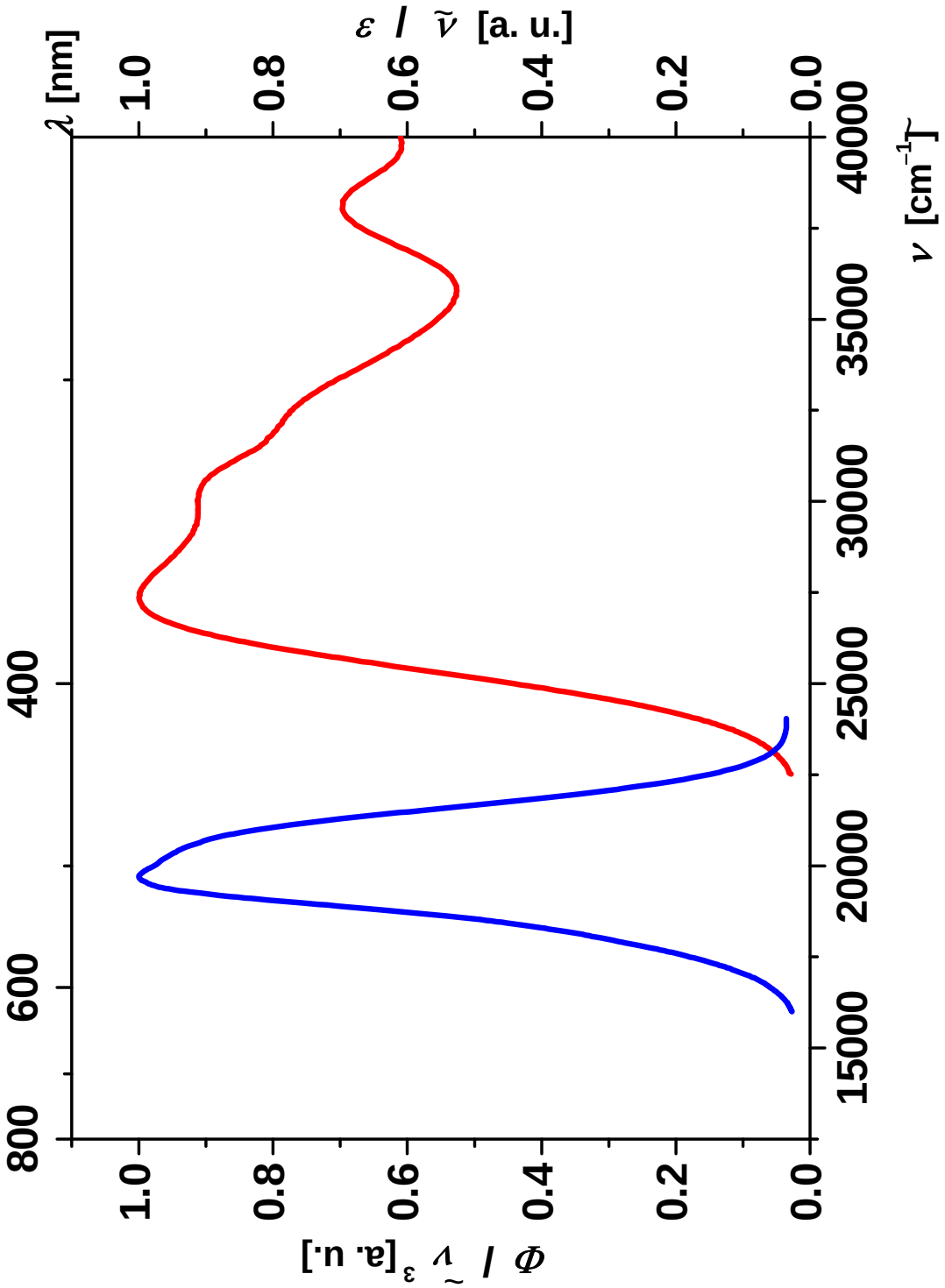
Compound 2h
(recorded in CH_2Cl_2, 20 °C)
Absorption



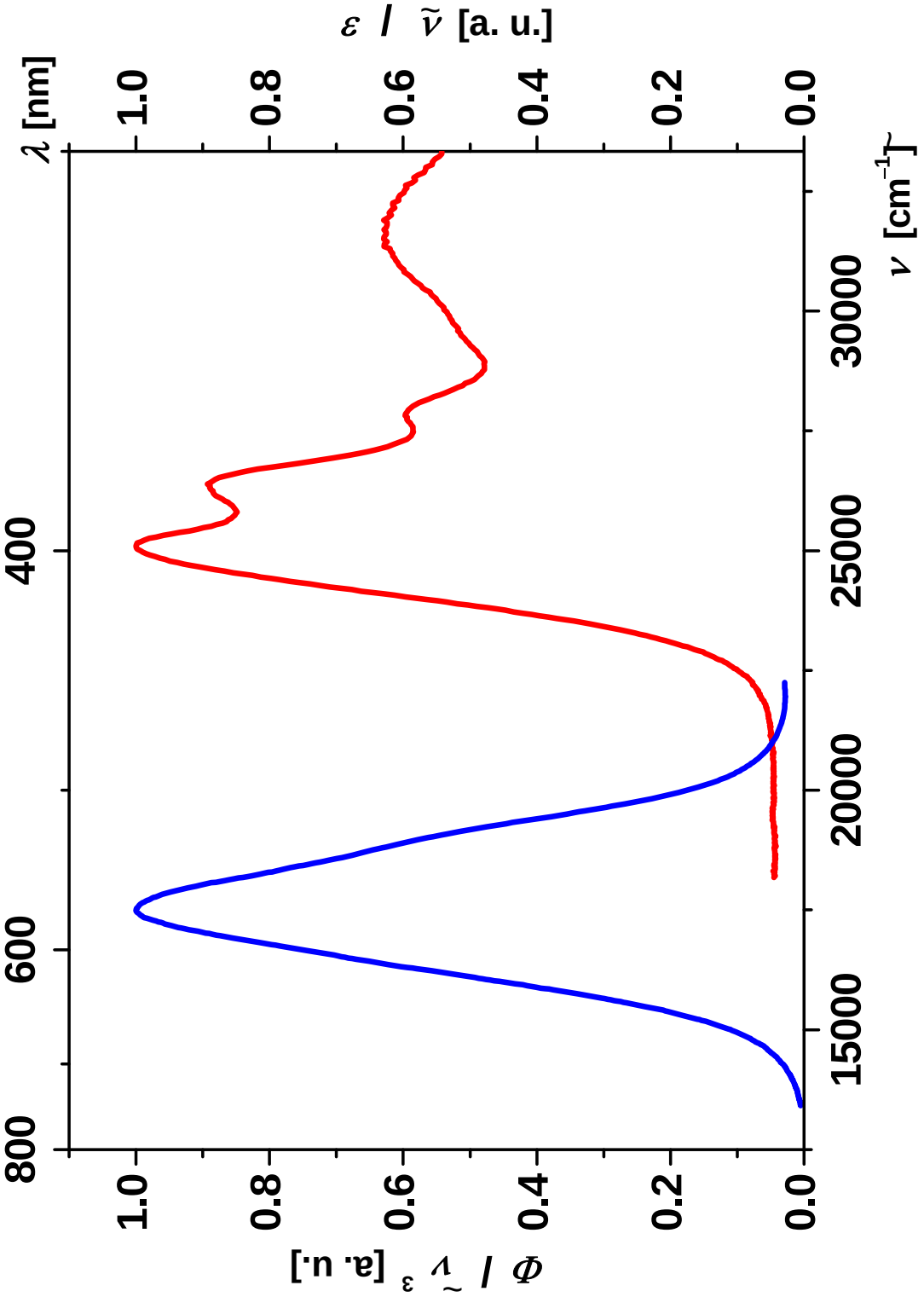
Emission


intensity [a. u.]
0
50
100
150
200
250
400
450
500
550
600
λ_{max} [nm]

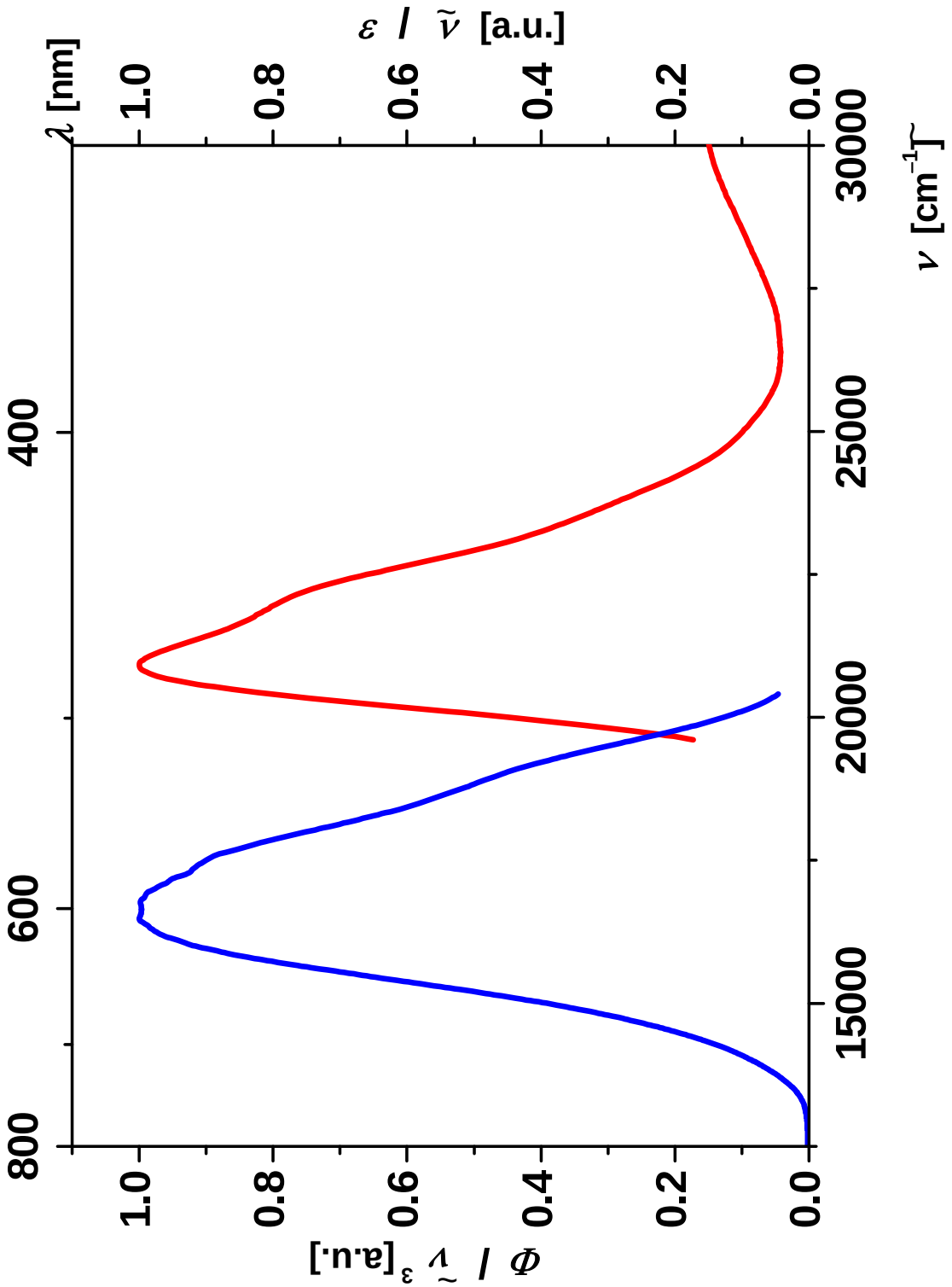
Compound 2i
(recorded in CH_2Cl_2, 20 °C, UV/Vis: *c*(**2i**) = 10^{-3} M; emission: *c*(**2i**) = 10^{-6} M)



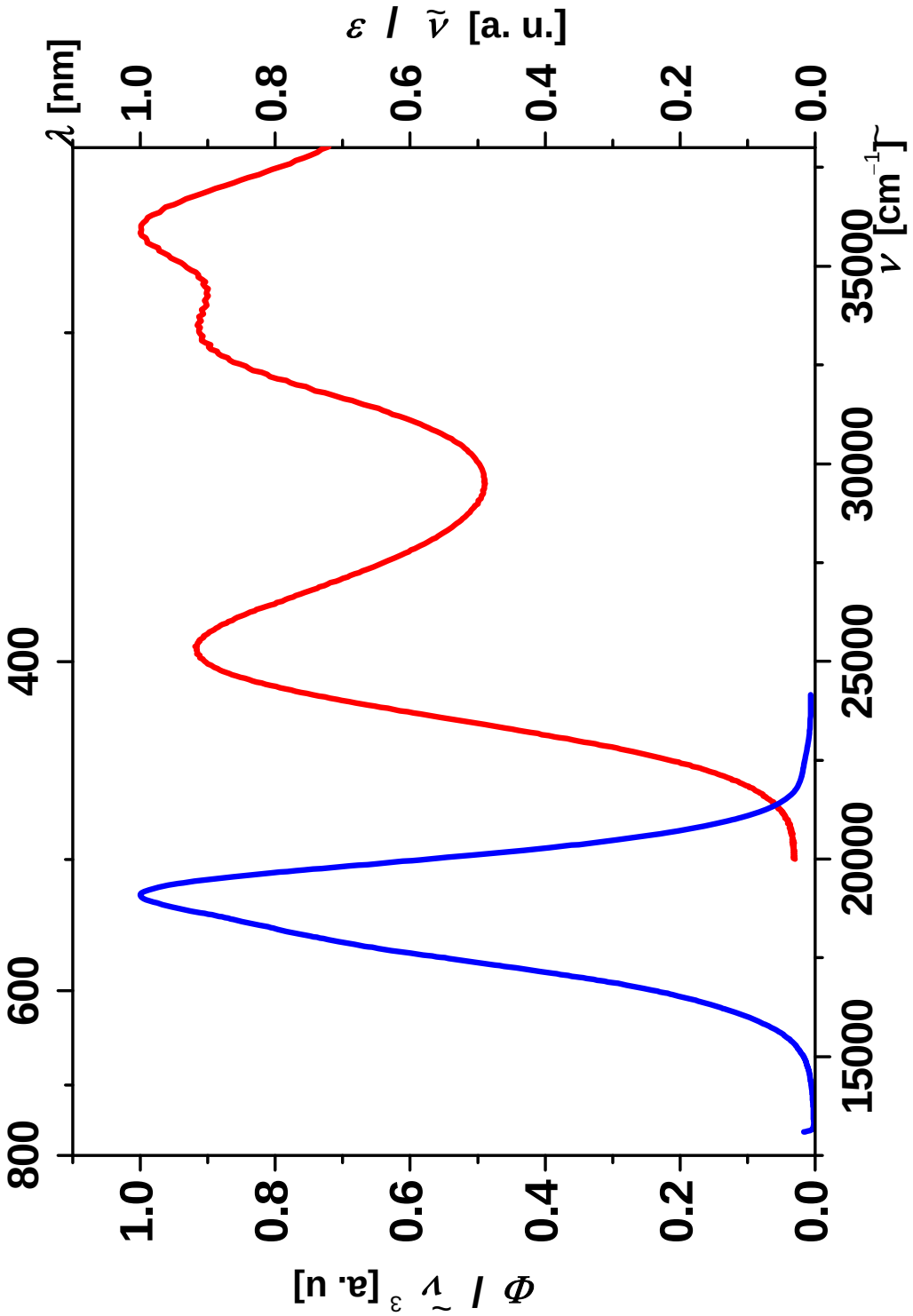
Compound 2j
(recorded in CH_2Cl_2, 20 °C, UV/Vis: c(**2j**) = 10^{-3} M; emission: c(**2j**) = 10^{-6} M)



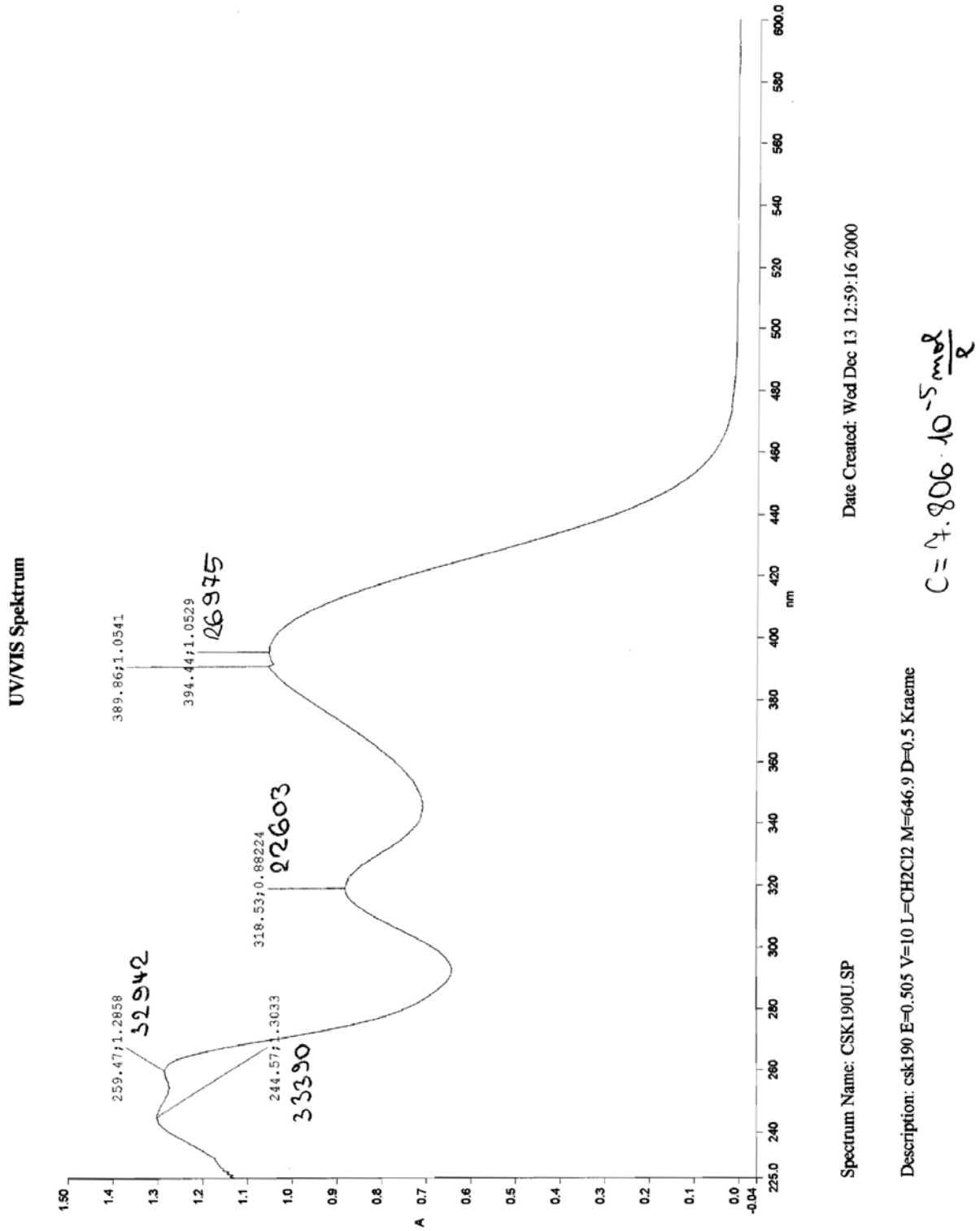
Compound 2k
(recorded in CH_2Cl_2, 20 °C, UV/Vis: *c*(**2k**) = 10^{-3} M; emission: *c*(**2k**) = 10^{-6} M)



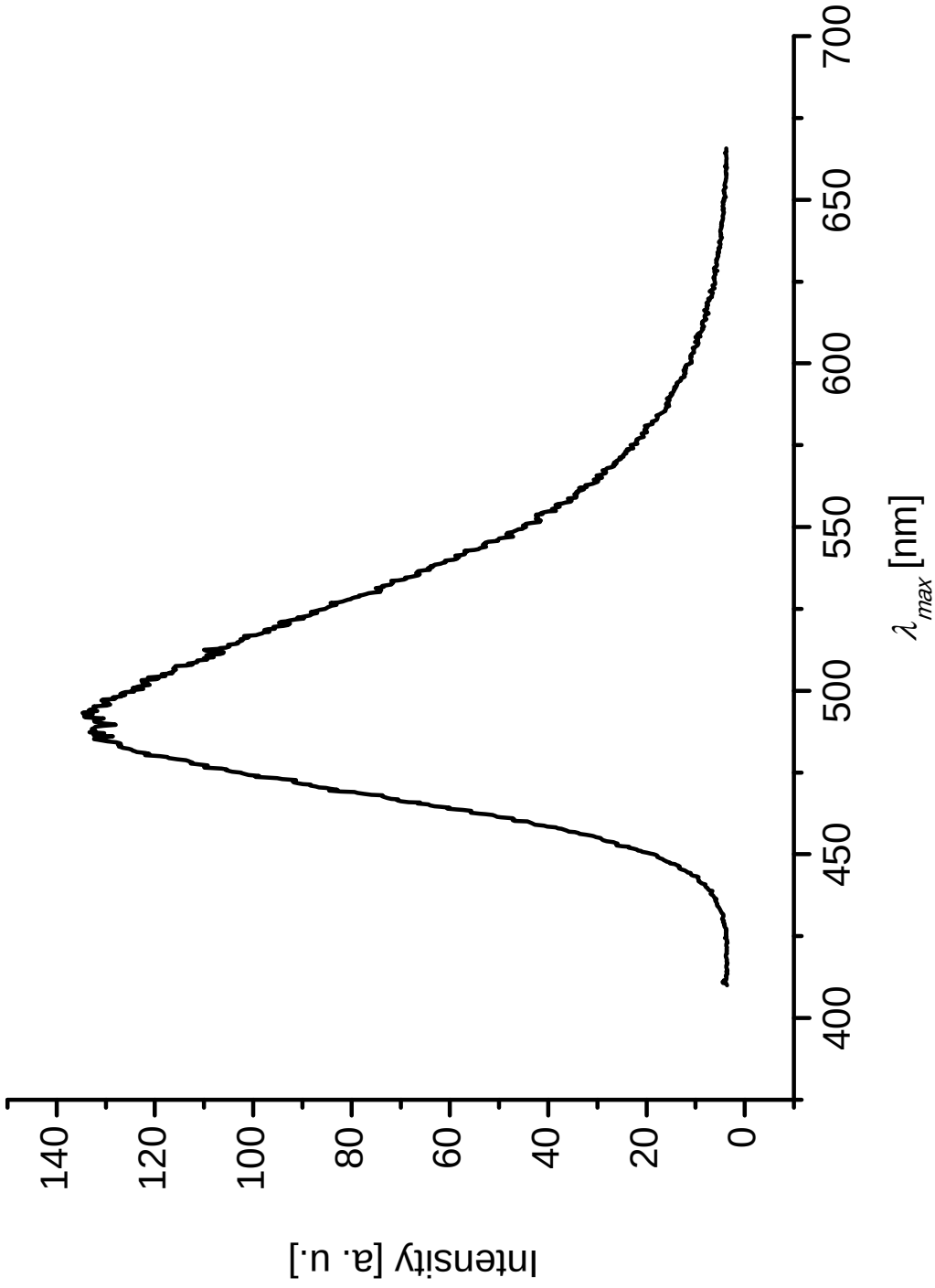
Compound 2l
(recorded in CH_2Cl_2, 20 °C, UV/Vis: c(**2l**) = 10^{-3} M; emission: c(**2l**) = 10^{-6} M)



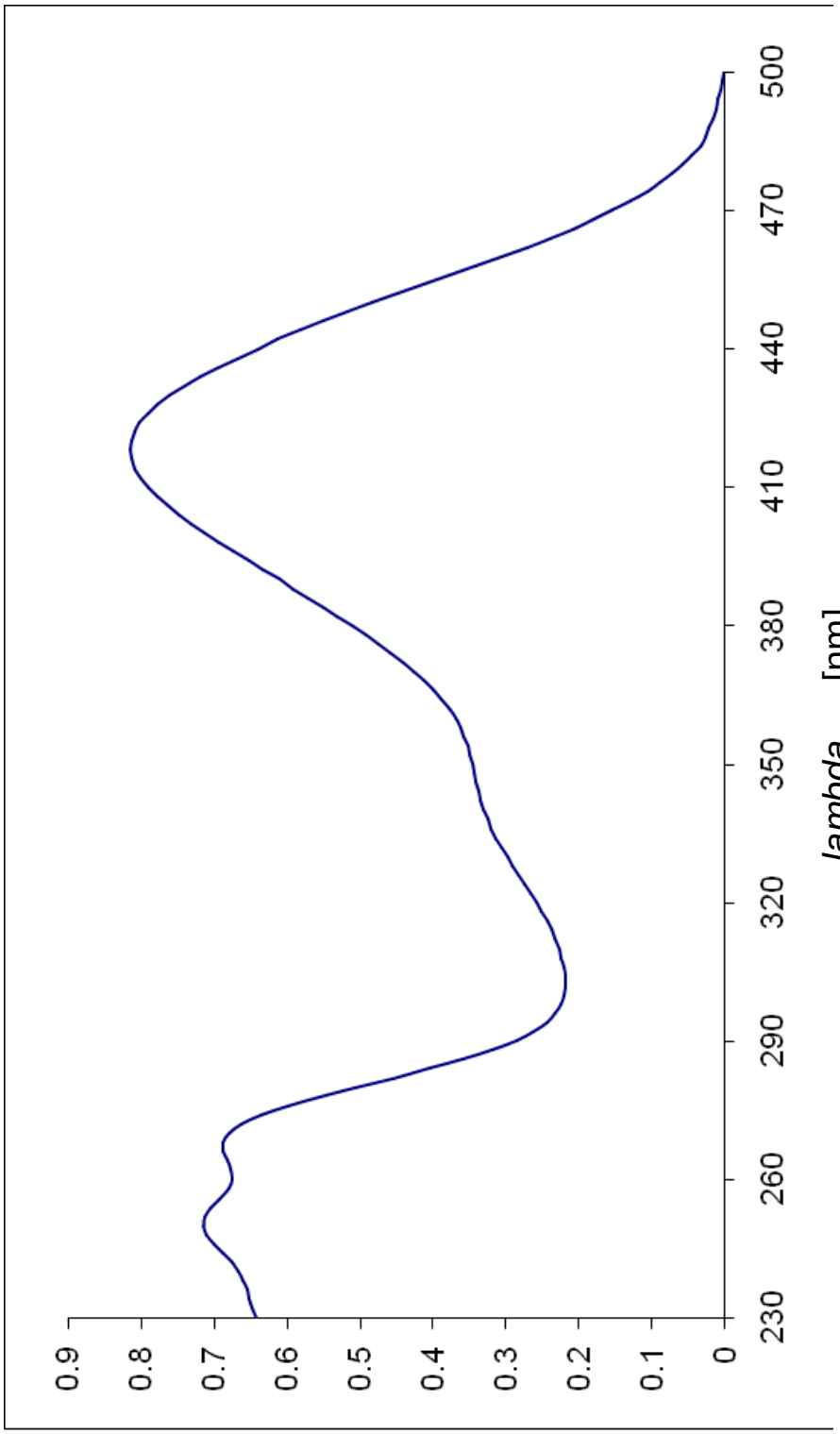
Compound 2m
(recorded in CH_2Cl_2, 20 °C)
Absorption



Emission

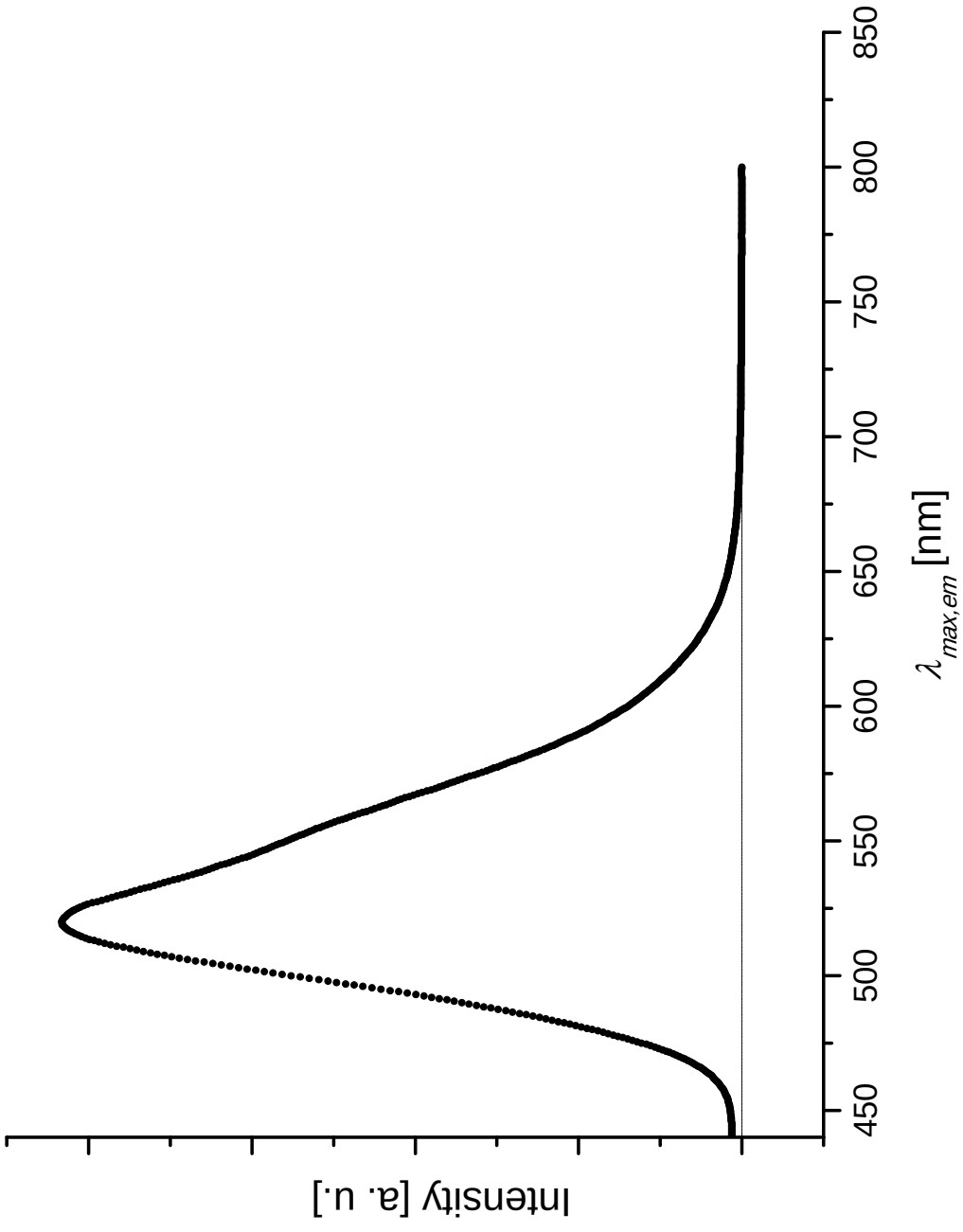

Intensity [a. u.]
0
20
40
60
80
100
120
140
400
450
500
550
600
650
700
λ_{max} [nm]

Compound 2n
(recorded in CH_2Cl_2, 20 °C)
Absorption

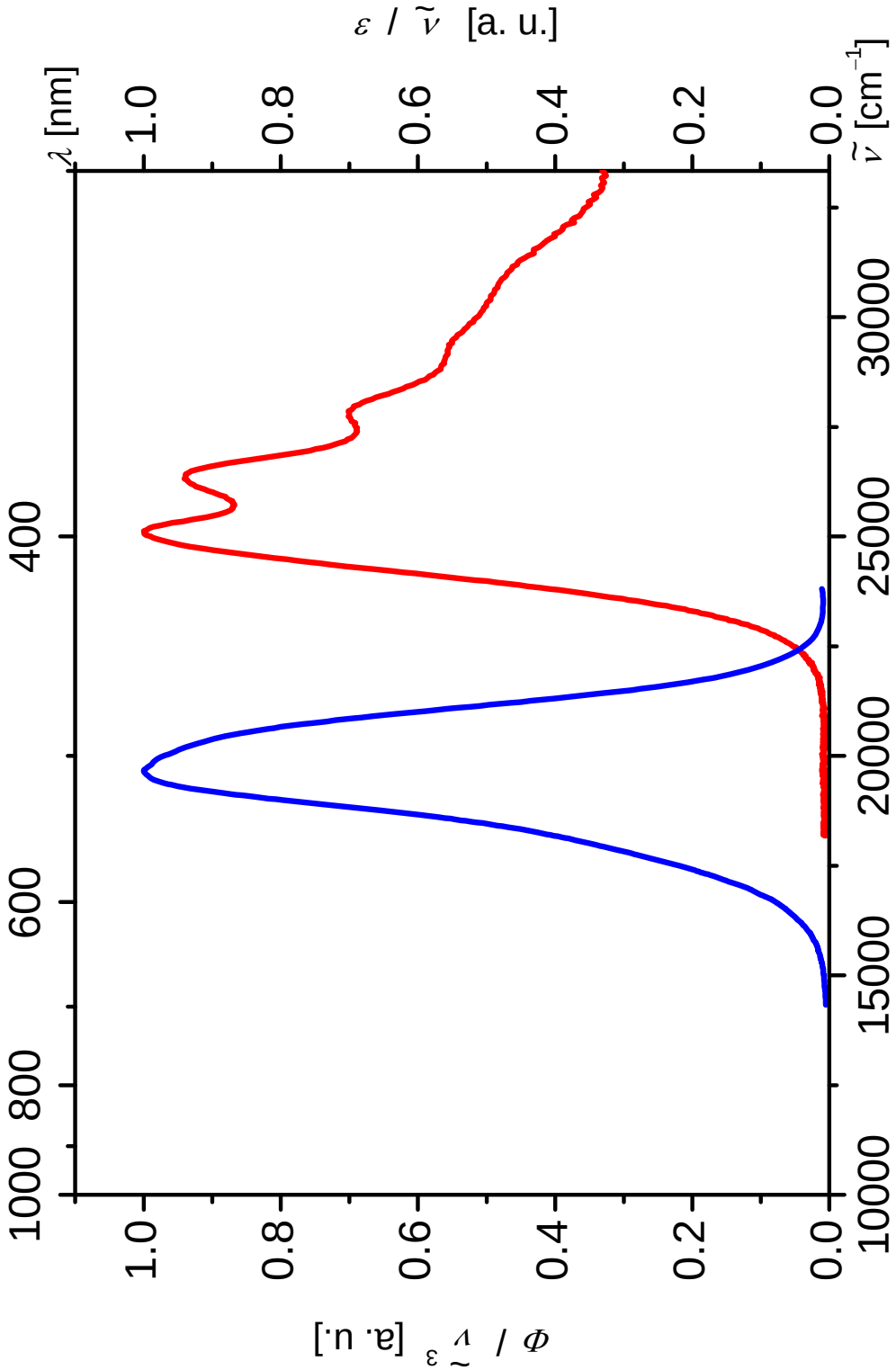


lambda$_{max}$ [nm]	log *eps*
250	4.58
266	4.57
338	4.25
418	4.64

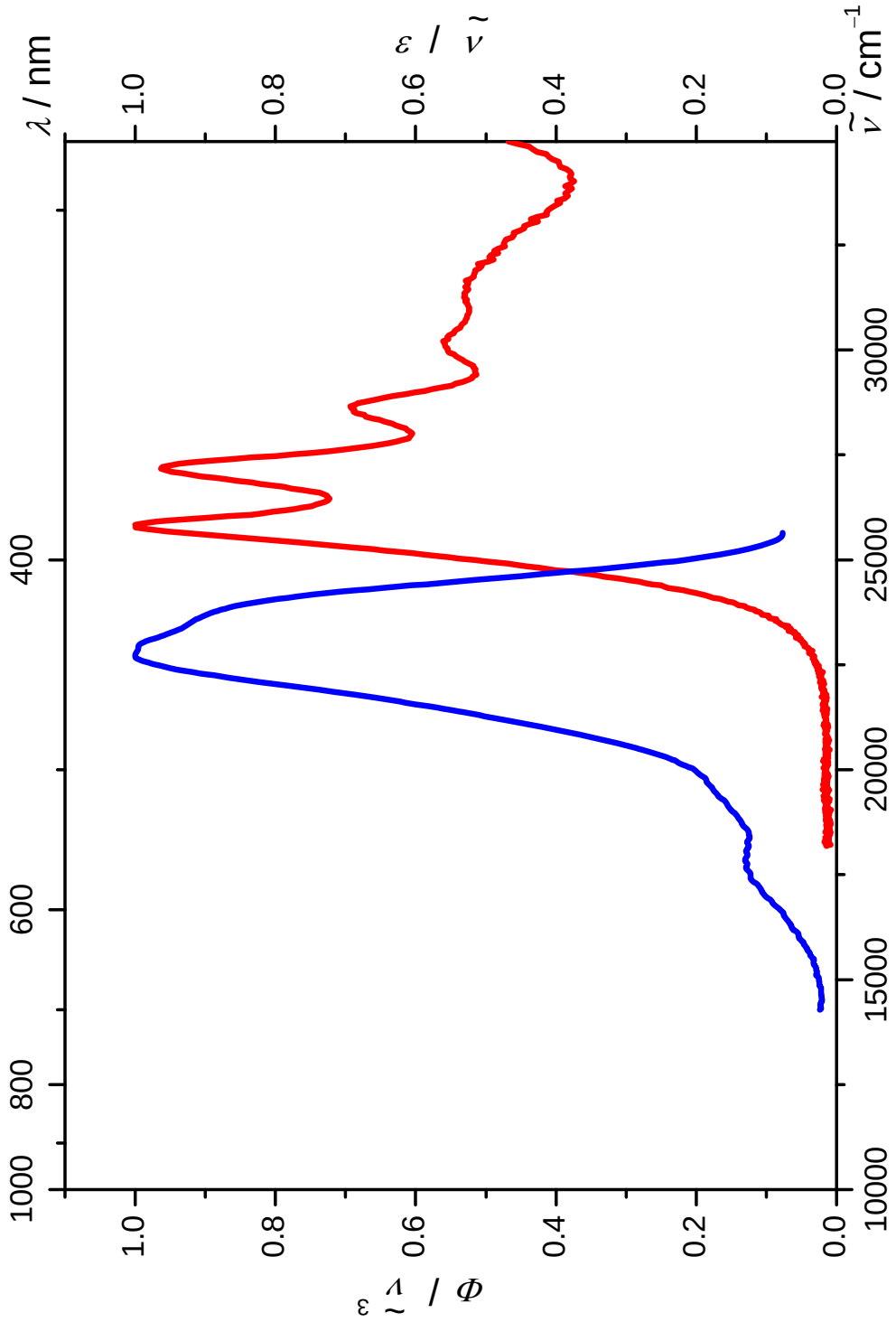
Emission


Intensity [a. u.]
450
500
550
600
650
700
750
800
850
$\lambda_{max,em}$ [nm]

Compound 2o
(recorded in dichloromethane, T = 298 K, UV/Vis: c(**2o**) = 10^{-3} M; emission: c(**2o**) = 10^{-6} M).



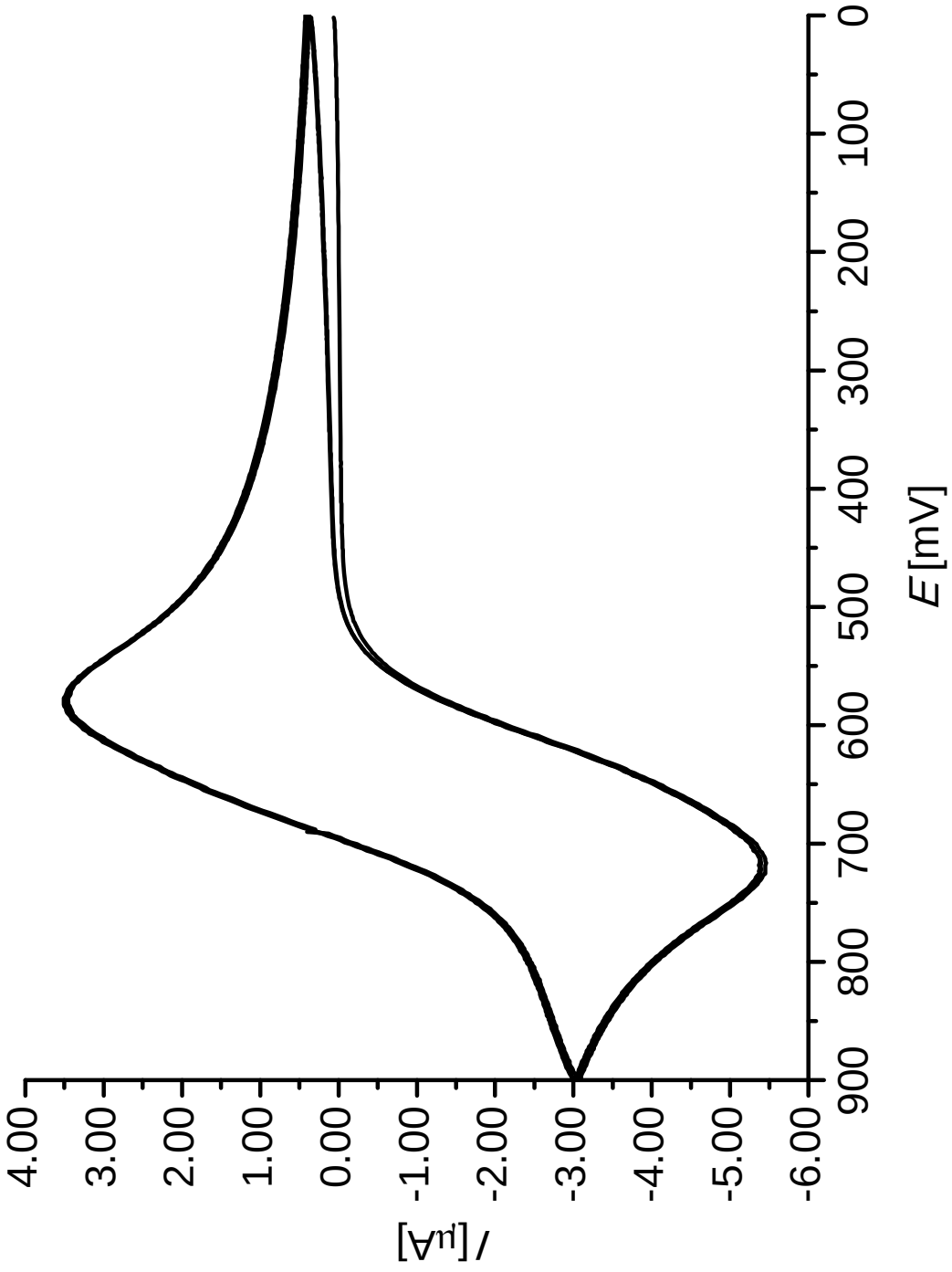
Compound 9
(recorded in dichloromethane, T = 298 K, UV/Vis: c(**9**) = 10^{-3} M; emission: c(**9**) = 10^{-6} M).



3. Cyclic voltammograms of compounds 2g-o, 7, and 9

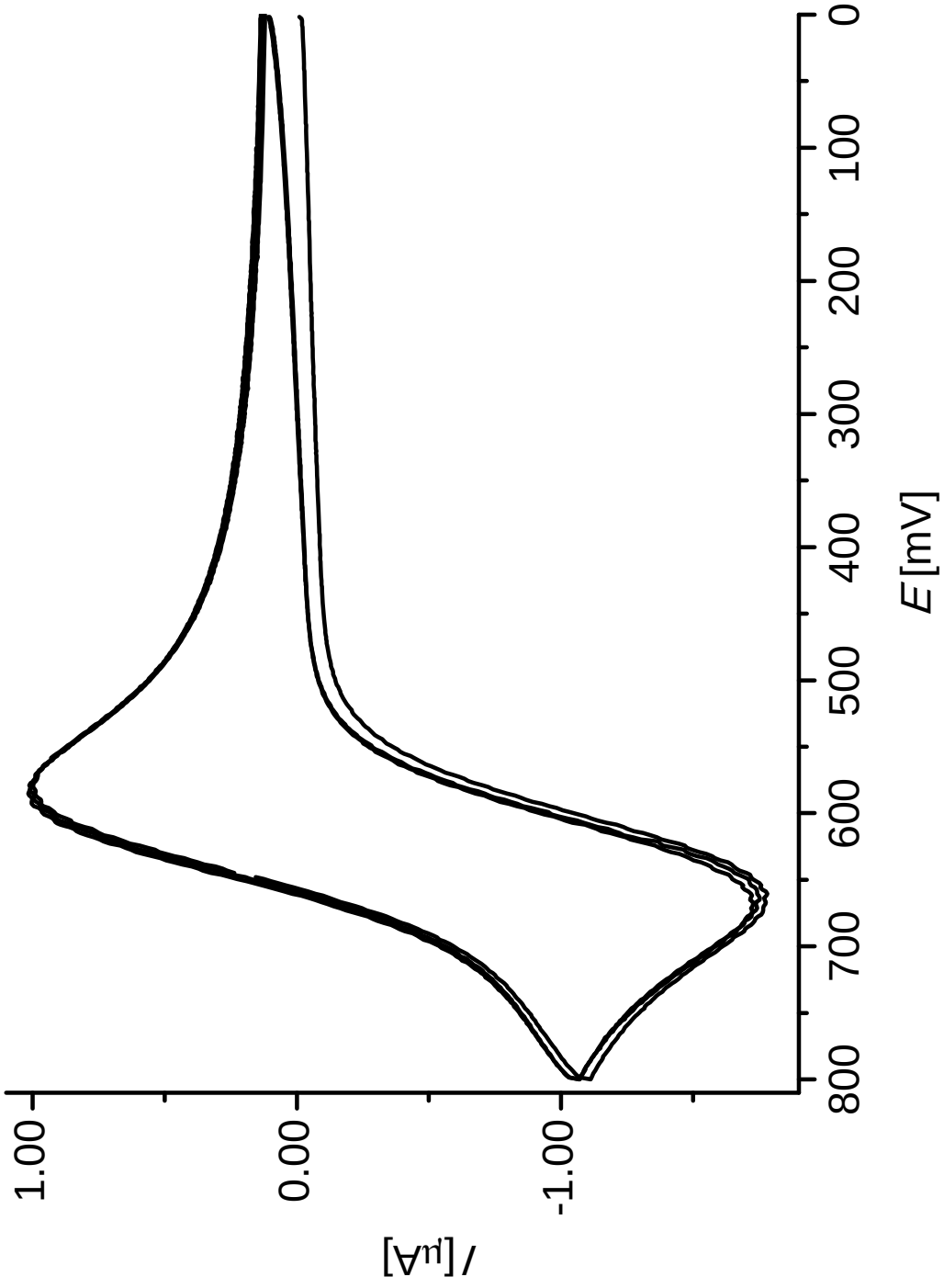
Compound 2g

(recorded in dichloromethane, T = 293 K, v = 100 mV/s, electrolyte: $^{n}Bu_4N^+$ PF_6^-, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).



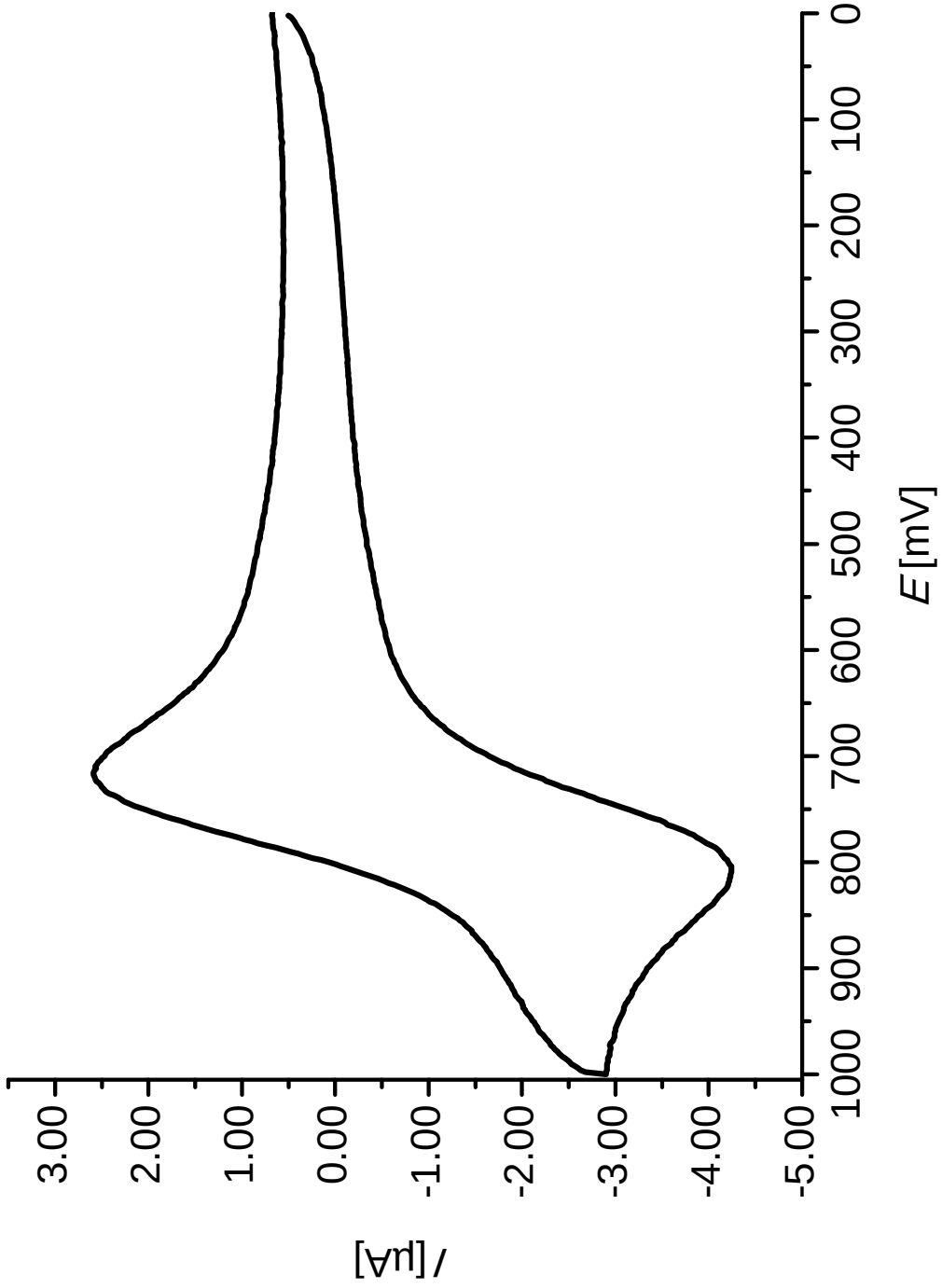
Compound 2h

(recorded in dichloromethane, T = 293 K, v = 100 mV/s, electrolyte: $^{n}Bu_4N^+$ PF_6^-, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).



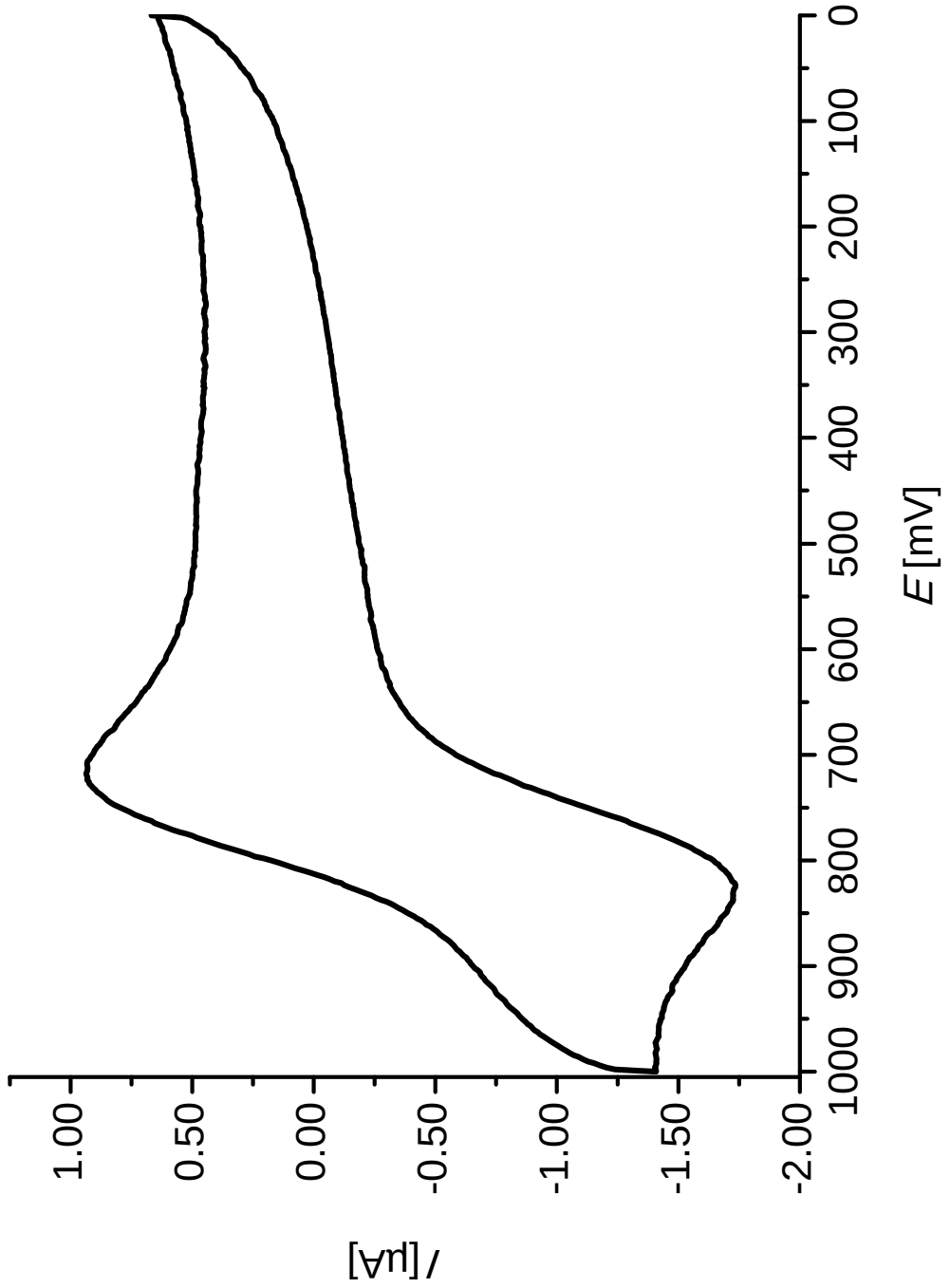
Compound 2i

(recorded in dichloromethane, T = 293 K, v = 100 mV/s, electrolyte: $^{n}Bu_4N^+$ PF_6^-, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).



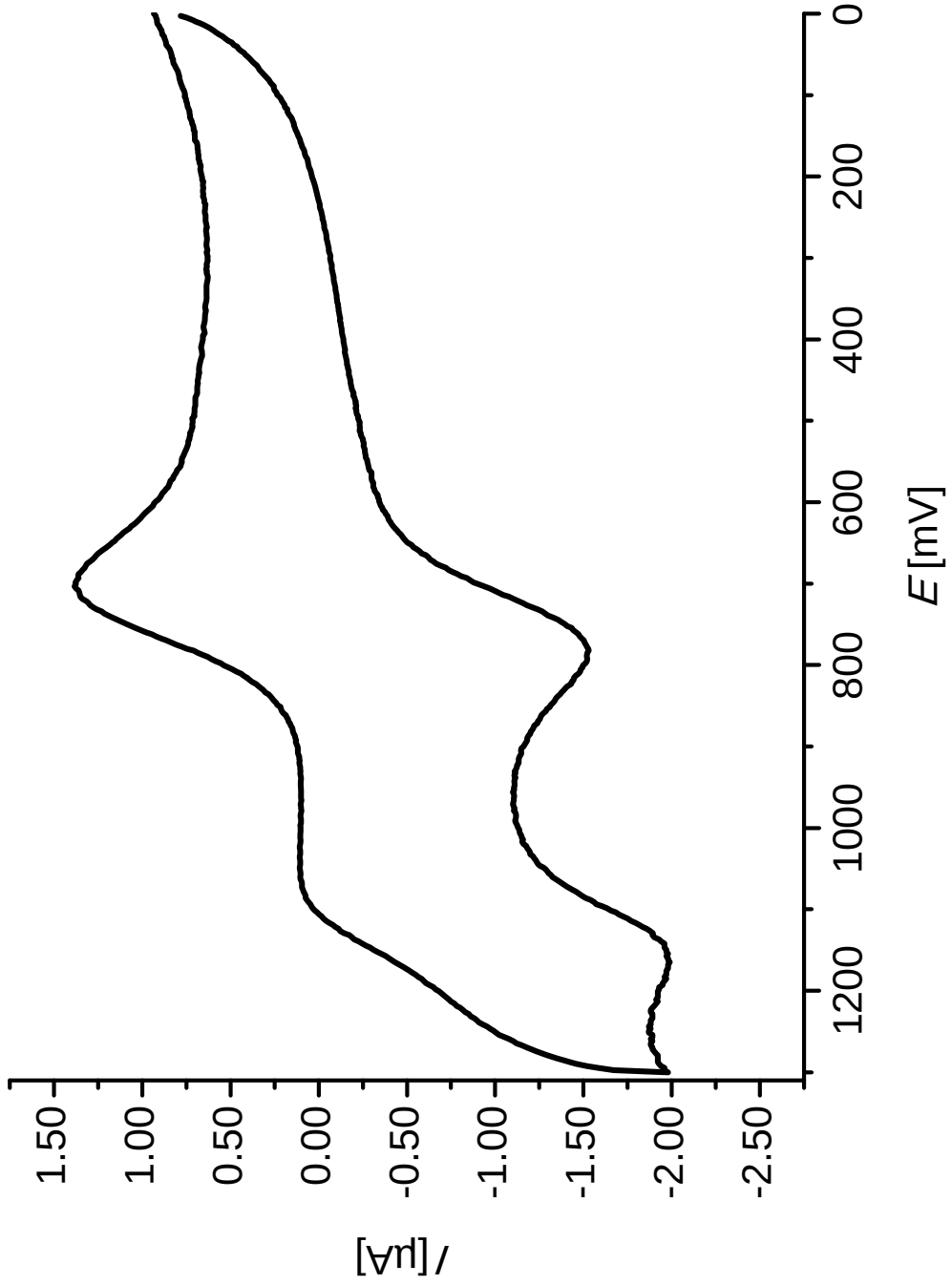
Compound 2j

(recorded in dichloromethane, T = 293 K, v = 100 mV/s, electrolyte: $^{n}Bu_4N^+$ PF_6^-, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).



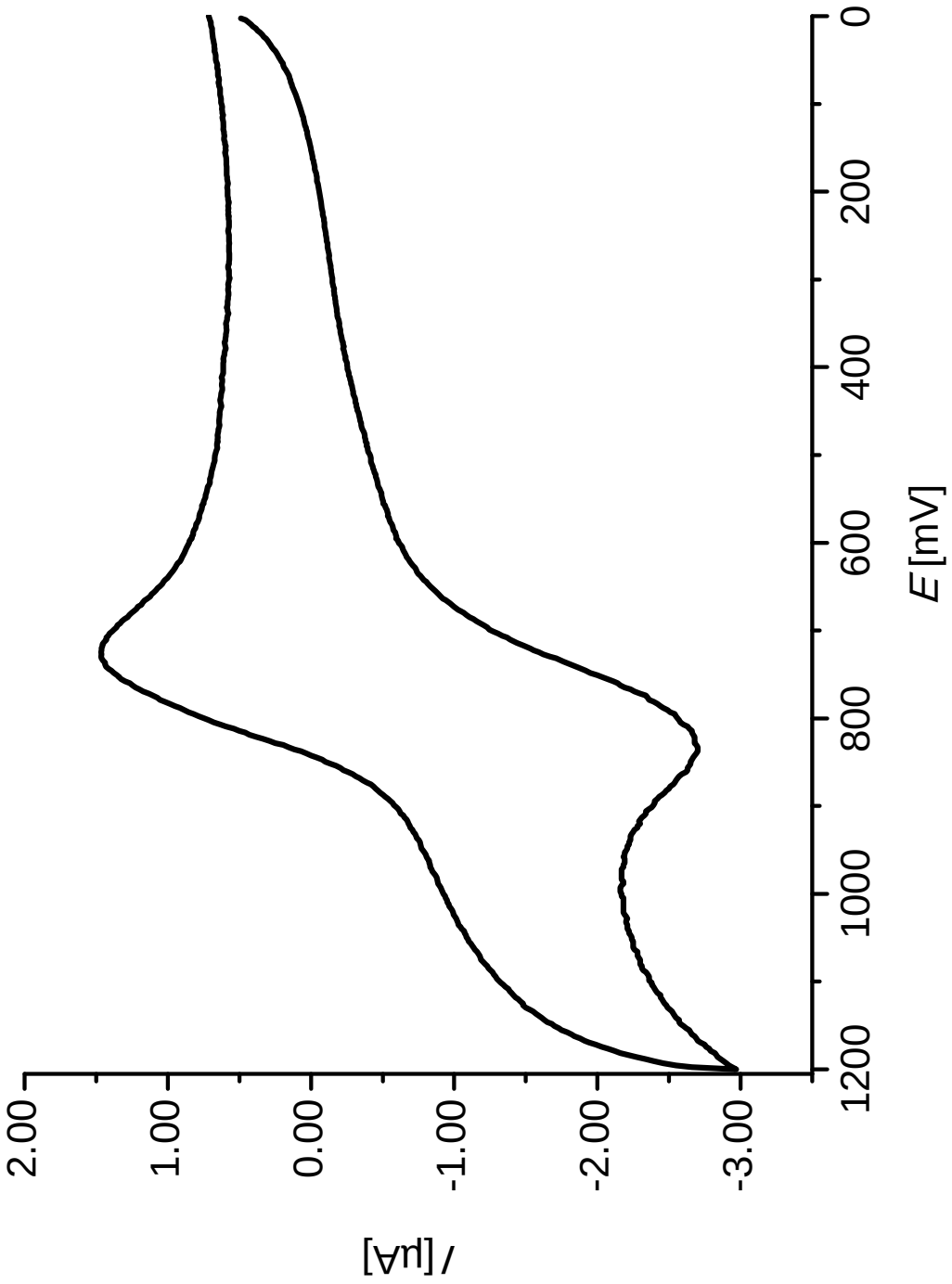
Compound 2k

(recorded in dichloromethane, T = 293 K, v = 100 mV/s, electrolyte: $^{n}Bu_4N^+$ PF_6^-, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).



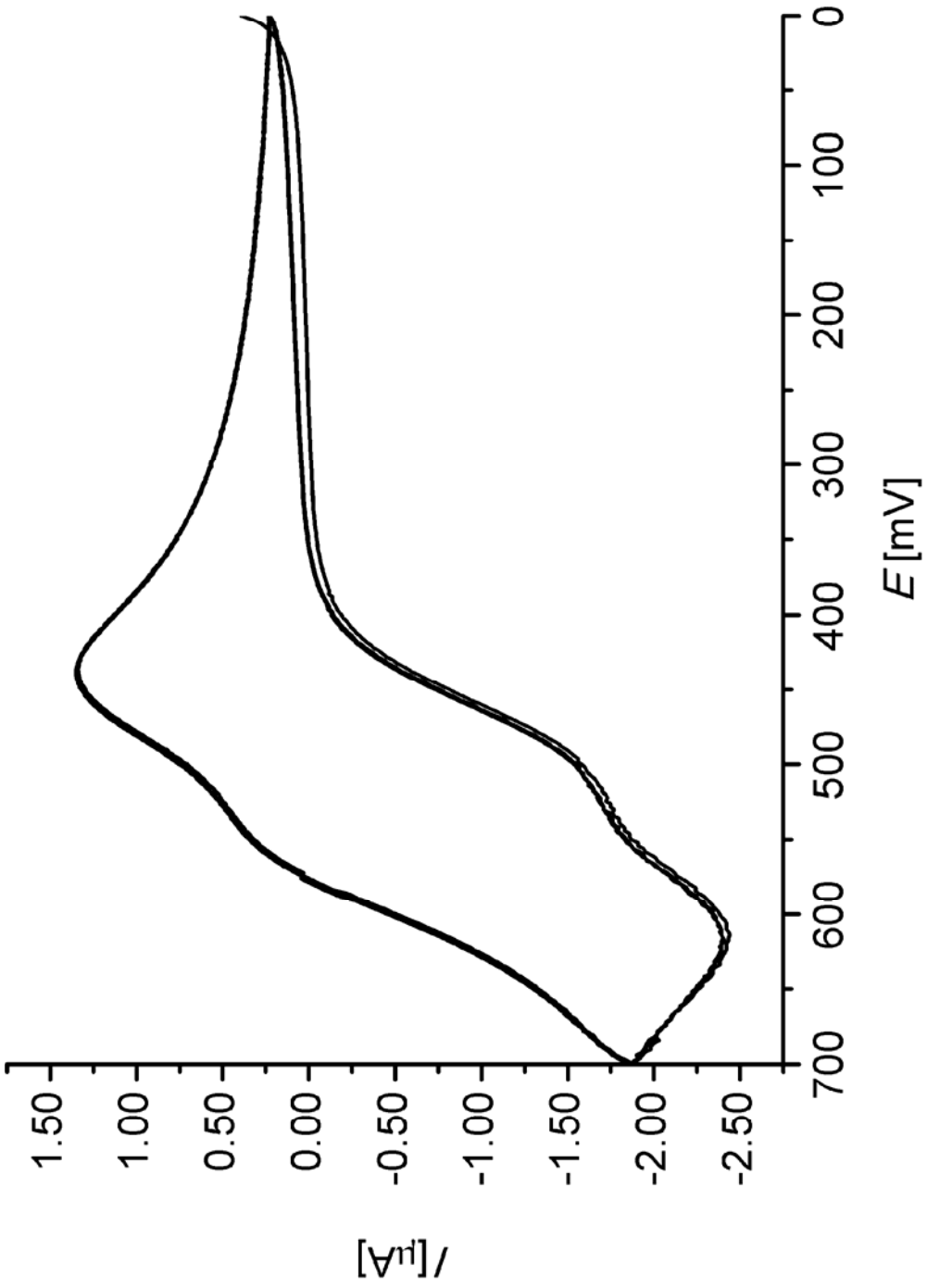
Compound 2l

(recorded in dichloromethane, T = 293 K, v = 100 mV/s, electrolyte: $^{n}Bu_4N^+$ PF_6^-, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).



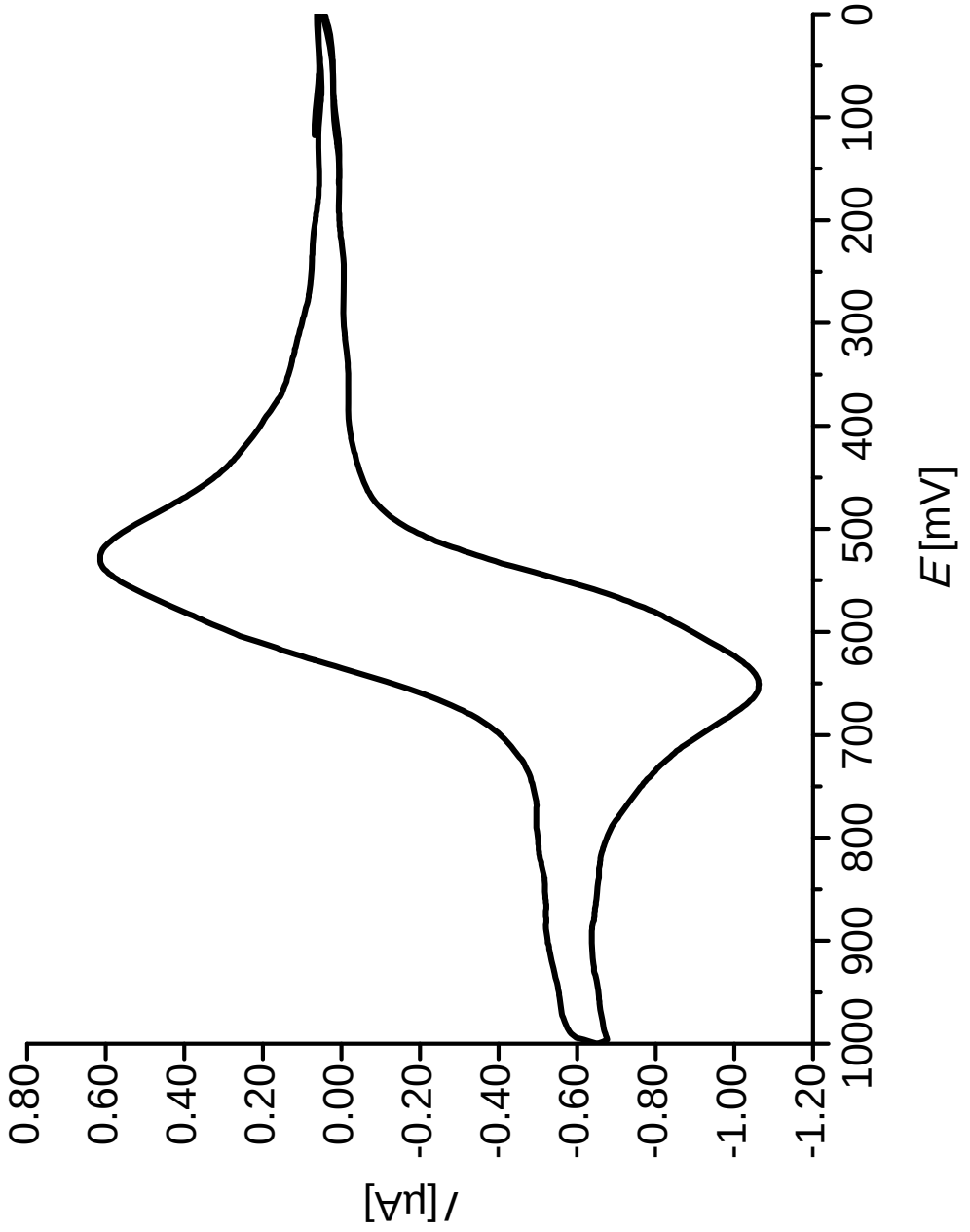
Compound 2m

(recorded in dichloromethane, T = 293 K, v = 100 mV/s, electrolyte: $^{n}Bu_4N^+$ PF_6^-, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).



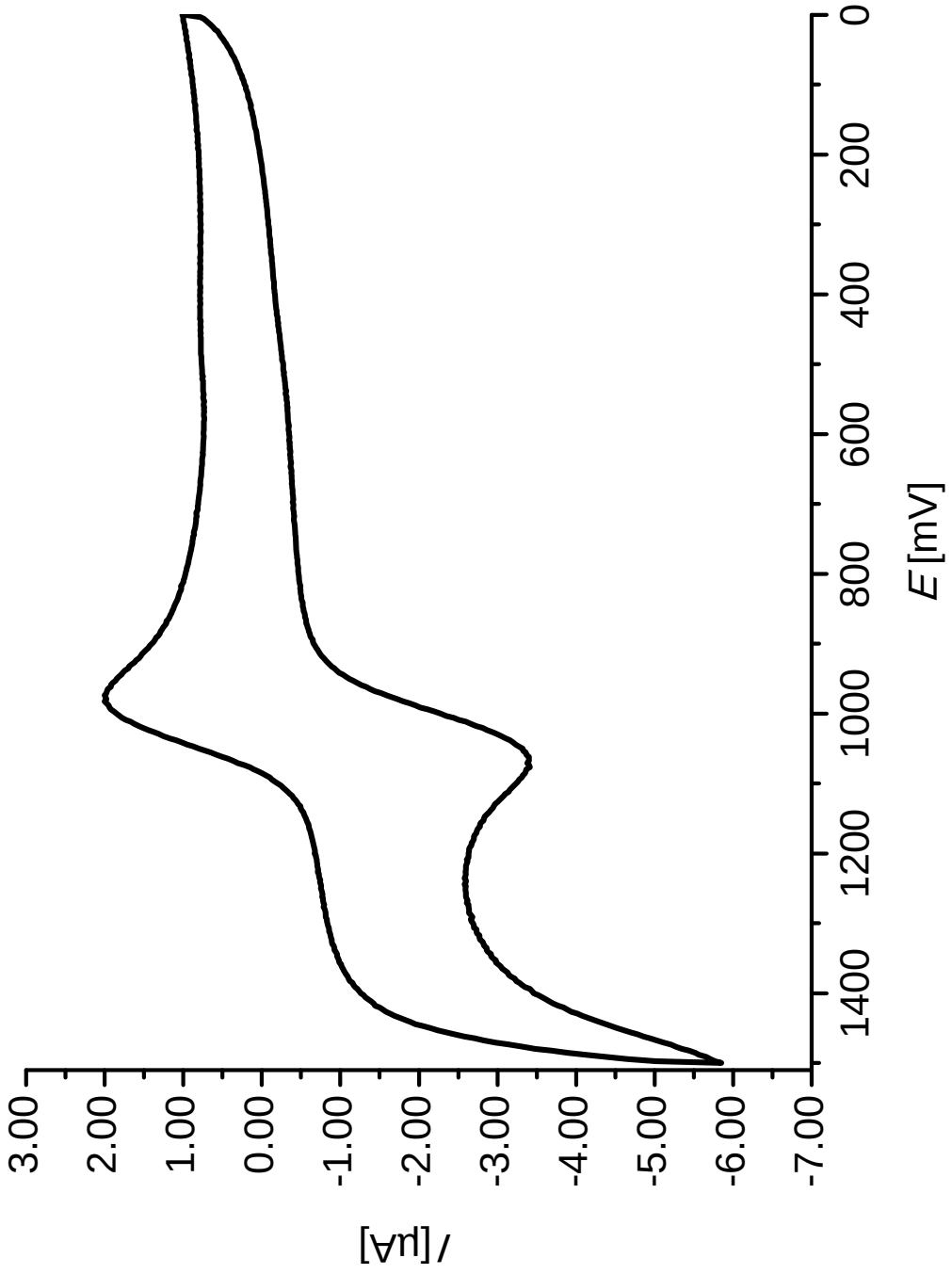
Compound 2n

(recorded in dichloromethane, T = 293 K, v = 100 mV/s, electrolyte: $^{n}Bu_4N^+$ PF_6^-, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).



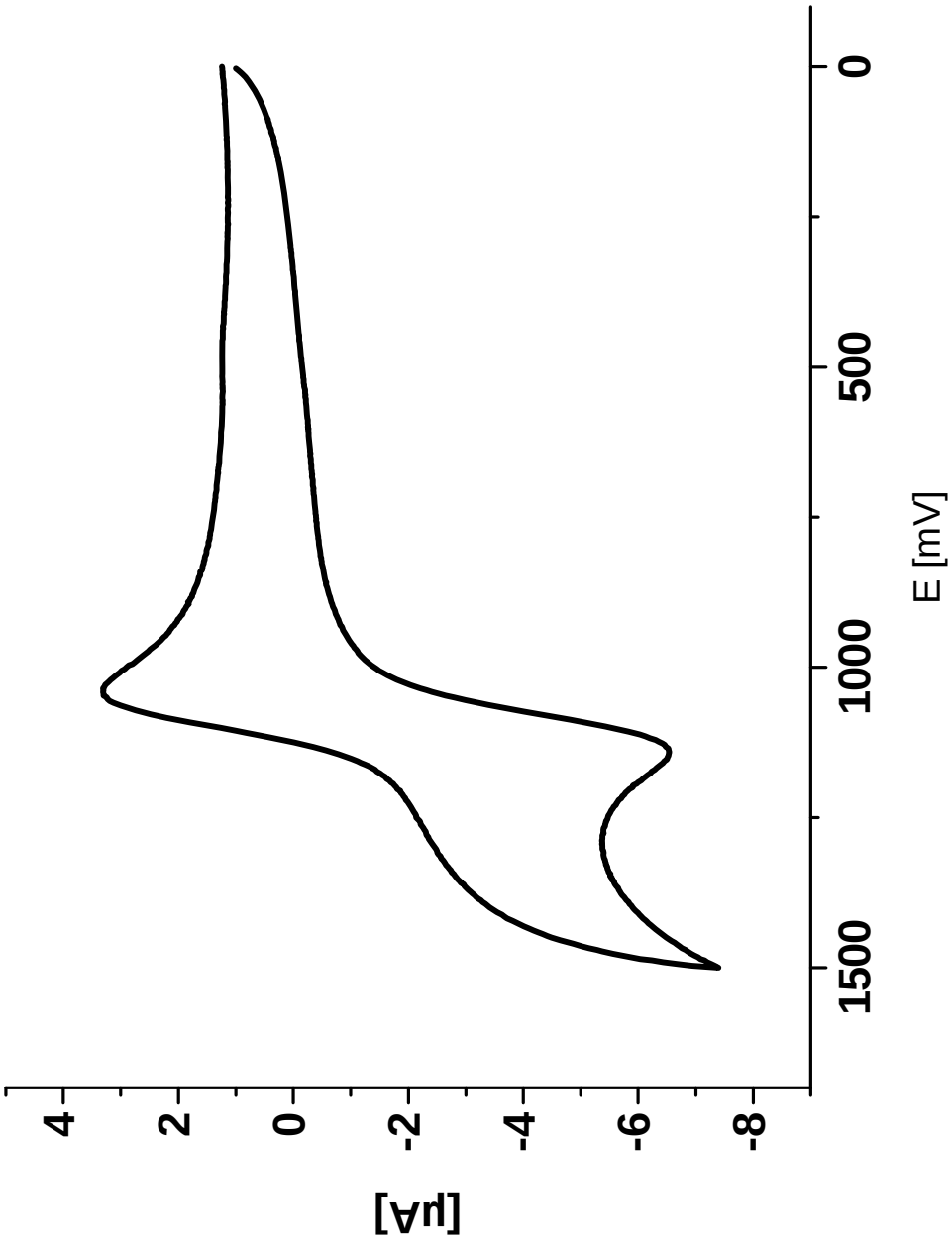
Compound 2o

(recorded in dichloromethane, T = 293 K, v = 100 mV/s, electrolyte: $^{n}Bu_4N^+$ PF_6^-, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).



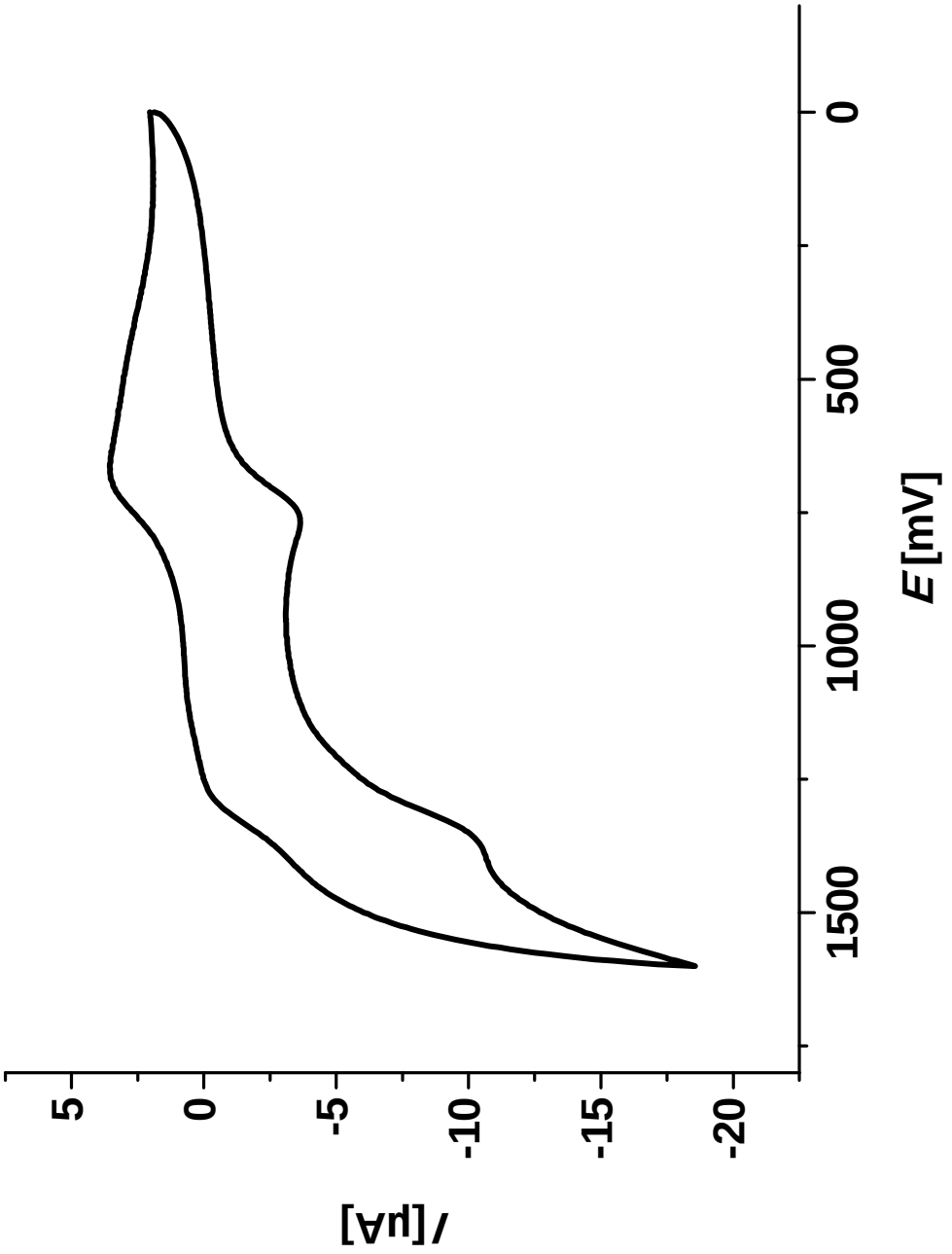
Compound 7

(recorded in dichloromethane, T = 293 K, ν = 100 mV/s, electrolyte: $^{n}Bu_4N^+$ PF_6^-, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).

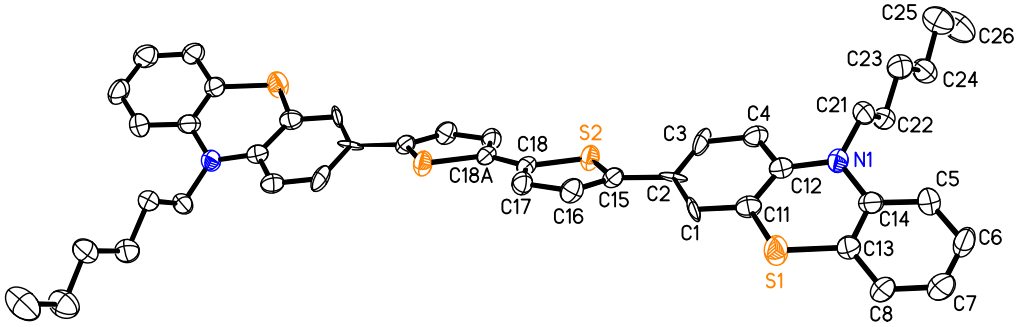


Compound 9

(recorded in dichloromethane, T = 293 K, v = 100 mV/s, electrolyte: $^{n}Bu_4N^+$ PF_6^-, Pt working electrode, Pt counter electrode, Ag/AgCl reference electrode).



4. Crystallographic data and figures of compound 2n



Empirical formula	$C_{44}H_{44}N_2S_4$	
Formula weight	729.05	
Temperature	200(2)	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P $\bar{1}$	
Z	1	
Unit cell dimensions	a = 9.923(2) Å	α = 87.174(6) °
	b = 14.160(3) Å	β = 63.147(8) °
	c = 7.3443(11) Å	γ = 83.720(6) °
Volume	915.2(3) $Å^3$	
Density (calculated)	1.323 g/cm^3	
Absorption coefficient μ	0.295 mm^{-1}	
Crystal form	polyhedron	
Crystal size	0.40 x 0.14 x 0.06 mm^3	
Theta range for data collection	1.45 to 20.93 °	
Index ranges	$-9 \le h \le 9$, $-14 \le k \le 14$, $-7 \le l \le 7$	
Reflections collected	8849	
Independent reflections	8849 (R(int) = 0.0000)	
Observed reflections	5681 ($I > 2\sigma(I)$)	
Absorption correction	Semi-empirical from equivalents	
Max/min transmission	0.98 and 0.89	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameter	8849 / 0 / 228	
Goodness-of-fit on F^2	0.95	
Final *R* indices ($I > 2\sigma(I)$)	R1 = 0.053, wR2 = 0.119	
Largest diff. peak and hole	0.31 and -0.25 $eÅ^{-3}$	

5. Molecular modeling coordinates and FMO energies of structures 2g-o

Structure 2g:

XYZ-Coordinates:

H	-1.871637	1.610751	-0.692799
C	-1.043930	0.910665	-0.676515
C	1.043930	-0.910665	-0.676515
C	0.271893	1.396311	-0.676535
C	-1.309418	-0.452588	-0.675105
C	-0.271893	-1.396311	-0.676535
C	1.309418	0.452588	-0.675105
H	-2.339206	-0.791079	-0.656202
H	2.339206	0.791079	-0.656202
H	1.871637	-1.610751	-0.692799
C	0.554843	2.851332	-0.678208
C	1.075919	5.646354	-0.699004
C	-0.233596	3.742425	0.064149
C	1.618785	3.388753	-1.412755
C	1.885605	4.753731	-1.411591
C	0.006387	5.110846	0.038363
H	-1.040244	3.364870	0.681314
H	2.243225	2.734033	-2.009313
H	2.726140	5.124008	-1.983901
C	-0.554843	-2.851332	-0.678208
C	-1.075919	-5.646354	-0.699004
C	0.233596	-3.742425	0.064149
C	-1.618785	-3.388753	-1.412755
C	-1.885605	-4.753731	-1.411591
C	-0.006387	-5.110846	0.038363
H	1.040244	-3.364870	0.681314
H	-2.243225	-2.734033	-2.009313
H	-2.726140	-5.124008	-1.983901
N	1.303110	7.042366	-0.687130
N	-1.303110	-7.042366	-0.687130
C	-1.217600	-7.713938	0.556127
C	-0.963131	-9.023134	3.037838
C	-0.160938	-7.406174	1.432246
C	-2.156494	-8.670446	0.965024
C	-2.016352	-9.331618	2.183504
C	-0.047476	-8.041585	2.665386
H	-3.007645	-8.897077	0.336423
H	-2.749382	-10.077631	2.468545
H	0.768822	-7.772337	3.325705
H	-0.858575	-9.529139	3.990118
C	1.217600	7.713938	0.556127
C	0.963131	9.023134	3.037838
C	0.160938	7.406174	1.432246
C	2.156494	8.670446	0.965024
C	2.016352	9.331618	2.183504
C	0.047476	8.041585	2.665386
H	3.007645	8.897077	0.336423
H	2.749382	10.077631	2.468545
H	-0.768822	7.772337	3.325705
H	0.858575	9.529139	3.990118
S	1.075919	-6.234130	0.904335
S	-1.075919	6.234130	0.904335
C	2.055526	7.655270	-1.785646
H	2.123639	8.719128	-1.563428
H	3.087527	7.278823	-1.832049

```
 C    -2.055526    -7.655270    -1.785646
 H    -2.123639    -8.719128    -1.563428
 H    -3.087527    -7.278823    -1.832049
 C    -1.360228    -7.494193    -3.139567
 H    -0.362211    -7.935943    -3.104625
 H    -1.257257    -6.448968    -3.433331
 H    -1.939791    -8.006996    -3.912184
 C     1.360228     7.494193    -3.139567
 H     0.362211     7.935943    -3.104625
 H     1.257257     6.448968    -3.433331
 H     1.939791     8.006996    -3.912184

SCF Done:  E(RB+HF-LYP) =  -2218.76704876     A.U. after    6 cycles
Sum of electronic and zero-point Energies=          -2218.239233
Sum of electronic and thermal Energies=             -2218.207589
Sum of electronic and thermal Enthalpies=           -2218.206645
Sum of electronic and thermal Free Energies=        -2218.303309
```

Structure 2h:

XYZ-Coordinates:

```
 H    -0.564802     1.030300     1.426164
 C    -0.177600     1.509473     0.534110
 C     0.766781     2.778205    -1.740359
 C     0.101506     0.734097    -0.601021
 C     0.013176     2.885168     0.533017
 C     0.489740     3.553641    -0.604597
 C     0.579597     1.402372    -1.737949
 H    -0.195436     3.448124     1.435738
 H     0.822957     0.834412    -2.628688
 H     1.117913     3.261888    -2.644757
 C     0.694411     5.020410    -0.608255
 C     1.089044     7.853393    -0.596319
 C     1.753374     5.613814    -1.301275
 C    -0.169880     5.879184     0.085709
 C     0.000562     7.257500     0.070450
 C     1.955675     6.989492    -1.283754
 H     2.464462     4.993046    -1.833488
 H    -1.027299     5.472065     0.609127
 H     2.810950     7.382310    -1.812392
 C    -0.101506    -0.734097    -0.601021
 C    -0.489740    -3.553641    -0.604597
 C    -0.579597    -1.402372    -1.737949
 C     0.177600    -1.509473     0.534110
 C    -0.013176    -2.885168     0.533017
 C    -0.766781    -2.778205    -1.740359
 H    -0.822957    -0.834412    -2.628688
 H     0.564802    -1.030300     1.426164
 H     0.195436    -3.448124     1.435738
 H    -1.117913    -3.261888    -2.644757
 C    -0.694411    -5.020410    -0.608255
 C    -1.089044    -7.853393    -0.596319
 C    -1.753374    -5.613814    -1.301275
 C     0.169880    -5.879184     0.085709
 C    -0.000562    -7.257500     0.070450
 C    -1.955675    -6.989492    -1.283754
 H    -2.464462    -4.993046    -1.833488
 H     1.027299    -5.472065     0.609127
 H    -2.810950    -7.382310    -1.812392
```

```
 N    -1.279161    -9.251569    -0.586852
 N     1.279161     9.251569    -0.586852
 C    -2.194937    -9.841843    -1.570376
 H    -2.042950    -9.306517    -2.510195
 H    -1.857551   -10.865289    -1.748093
 C     2.194937     9.841843    -1.570376
 H     2.042950     9.306517    -2.510195
 H     1.857551    10.865289    -1.748093
 C     3.690660     9.844020    -1.212095
 H     4.255985    10.307878    -2.025862
 H     4.080377     8.836290    -1.064024
 H     3.895037    10.403987    -0.298947
 C    -3.690660    -9.844020    -1.212095
 H    -4.255985   -10.307878    -2.025862
 H    -4.080377    -8.836290    -1.064024
 H    -3.895037   -10.403987    -0.298947
 C    -0.825664   -10.054413     0.484619
 C     0.086185   -11.650083     2.639823
 C    -1.450813   -11.267377     0.814957
 C     0.291223    -9.674841     1.255030
 C     0.716776   -10.447343     2.331784
 C    -0.991266   -12.059105     1.865362
 H    -2.305372   -11.610835     0.252009
 H     1.566723   -10.109368     2.913731
 H    -1.496843   -12.993716     2.079538
 H     0.437077   -12.252988     3.468533
 C     0.825664    10.054413     0.484619
 C    -0.086185    11.650083     2.639823
 C     1.450813    11.267377     0.814957
 C    -0.291223     9.674841     1.255030
 C    -0.716776    10.447343     2.331784
 C     0.991266    12.059105     1.865362
 H     2.305372    11.610835     0.252009
 H    -1.566723    10.109368     2.913731
 H     1.496843    12.993716     2.079538
 H    -0.437077    12.252988     3.468533
 S     1.279161    -8.276548     0.771025
 S    -1.279161     8.276548     0.771025

SCF Done:  E(RB+HF-LYP) =  -2449.87439717     A.U. after    7 cycles
Sum of electronic and zero-point Energies=          -2449.265286
Sum of electronic and thermal Energies=             -2449.228959
Sum of electronic and thermal Enthalpies=           -2449.228015
Sum of electronic and thermal Free Energies=        -2449.335932
```

Structure 2i:

XYZ-Coordinates:

```
 H    -2.671547    -0.683812     1.330485
 C    -1.654971    -0.493856     1.657219
 C     0.971251    -0.024918     2.538014
 C    -0.626037    -0.316443     0.732554
 C    -1.363207    -0.436869     3.015870
 C    -0.056858    -0.202370     3.481355
 C     0.687233    -0.083101     1.183696
 H    -2.157028    -0.603282     3.734912
 H     1.979742     0.185329     2.878259
 C    -0.626037    -0.316443    -0.732554
 C    -0.056858    -0.202370    -3.481355
```

C	-1.654971	-0.493856	-1.657219
C	0.687233	-0.083101	-1.183696
C	0.971251	-0.024918	-2.538014
C	-1.363207	-0.436869	-3.015870
H	-2.671547	-0.683812	-1.330485
H	1.979742	0.185329	-2.878259
H	-2.157028	-0.603282	-3.734912
C	1.617036	0.088787	0.000000
H	2.099031	1.073180	0.000000
H	2.420100	-0.657165	0.000000
C	0.232173	-0.143914	-4.934264
C	0.792645	-0.012640	-7.719433
C	-0.665803	0.457136	-5.828681
C	1.404736	-0.691783	-5.469122
C	1.673312	-0.643980	-6.832742
C	-0.384295	0.540562	-7.186408
H	-1.580521	0.903910	-5.457220
H	2.103792	-1.200853	-4.815896
H	2.575183	-1.111227	-7.206386
C	0.232173	-0.143914	4.934264
C	0.792645	-0.012640	7.719433
C	1.404736	-0.691783	5.469122
C	-0.665803	0.457136	5.828681
C	-0.384295	0.540562	7.186408
C	1.673312	-0.643980	6.832742
H	2.103792	-1.200853	4.815896
H	-1.580521	0.903910	5.457220
H	2.575183	-1.111227	7.206386
N	1.038796	0.073257	-9.108754
N	1.038796	0.073257	9.108754
C	2.413769	-0.044927	-9.602797
H	2.365043	0.034642	-10.687699
H	2.841716	-1.032929	-9.380336
C	2.413769	-0.044927	9.602797
H	2.841716	-1.032929	9.380336
H	2.365043	0.034642	10.687699
C	-0.040129	-0.181827	-9.989173
C	-2.230499	-0.623411	-11.705134
C	-1.303823	0.366977	-9.705568
C	0.091768	-0.977753	-11.134770
C	-0.987669	-1.177205	-11.992938
C	-2.388647	0.132228	-10.545521
H	1.037744	-1.453603	-11.357867
H	-0.853699	-1.785990	-12.879804
H	-3.353941	0.555385	-10.292500
H	-3.073621	-0.785607	-12.365918
C	-0.040129	-0.181827	9.989173
C	-2.230499	-0.623411	11.705134
C	0.091768	-0.977753	11.134770
C	-1.303823	0.366977	9.705568
C	-2.388647	0.132228	10.545521
C	-0.987669	-1.177205	11.992938
H	1.037744	-1.453603	11.357867
H	-3.353941	0.555385	10.292500
H	-0.853699	-1.785990	12.879804
H	-3.073621	-0.785607	12.365918
S	-1.476612	1.429650	8.282754
S	-1.476612	1.429650	-8.282754
C	3.326514	1.068603	9.083628
H	2.928744	2.044683	9.369063
H	3.430264	1.049913	7.998162
H	4.322907	0.958830	9.520649

```
 C     3.326514     1.068603    -9.083628
 H     2.928744     2.044683    -9.369063
 H     4.322907     0.958830    -9.520649
 H     3.430264     1.049913    -7.998162

SCF Done:  E(RB+HF-LYP) =  -2487.99821758     A.U. after    6 cycles
Sum of electronic and zero-point Energies=          -2487.383661
Sum of electronic and thermal Energies=             -2487.347030
Sum of electronic and thermal Enthalpies=           -2487.346086
Sum of electronic and thermal Free Energies=        -2487.455599
```

Structure 2j:

XYZ-Coordinates:

```
 H    -3.434888    -2.595357     1.247143
 C    -2.616924    -2.127987     0.710296
 H    -1.595553    -1.550793     2.482137
 C    -1.591999    -1.544925     1.400090
 C    -1.591999    -1.544925    -1.400090
 C    -0.497979    -0.917161     0.722478
 C    -2.616924    -2.127987    -0.710296
 C    -0.497979    -0.917161    -0.722478
 C     0.564840    -0.316275     1.426961
 H    -3.434888    -2.595357    -1.247143
 H    -1.595553    -1.550793    -2.482137
 C     1.625637     0.287794     0.722433
 C     2.717611     0.919188     1.399852
 C     1.625637     0.287794    -0.722433
 H     2.719184     0.927269    -2.481950
 C     0.564840    -0.316275    -1.426961
 C     3.740125     1.506800     0.710335
 H     2.719184     0.927269     2.481950
 H     4.554723     1.980211     1.247058
 C     3.740125     1.506800    -0.710335
 H     4.554723     1.980211    -1.247058
 C     2.717611     0.919188    -1.399852
 C     0.567020    -0.322085    -2.923458
 C     0.575144    -0.326377    -5.759120
 C    -0.119736     0.660466    -3.645014
 C     1.241445    -1.312538    -3.641198
 C     1.233415    -1.326667    -5.033858
 C    -0.100129     0.672101    -5.036399
 H    -0.665157     1.433507    -3.115903
 H     1.769034    -2.093036    -3.104858
 H     1.746400    -2.124880    -5.554254
 C     0.567020    -0.322085     2.923458
 C     0.575144    -0.326377     5.759120
 C    -0.119736     0.660466     3.645014
 C     1.241445    -1.312538     3.641198
 C     1.233415    -1.326667     5.033858
 C    -0.100129     0.672101     5.036399
 H    -0.665157     1.433507     3.115903
 H     1.769034    -2.093036     3.104858
 H     1.746400    -2.124880     5.554254
 N     0.555317    -0.296613    -7.173527
 N     0.555317    -0.296613     7.173527
 C    -0.677630    -0.014021    -7.809514
 C    -3.131786     0.627927    -9.034895
```

C	-1.485291	1.024509	-7.312097
C	-1.141524	-0.739168	-8.915138
C	-2.345357	-0.405610	-9.532398
C	-2.705904	1.328002	-7.908276
H	-0.567706	-1.574199	-9.295221
H	-2.673305	-0.973668	-10.395464
H	-3.313529	2.123627	-7.492827
H	-4.072950	0.882118	-9.507544
C	-0.677630	-0.014021	7.809514
C	-3.131786	0.627927	9.034895
C	-1.485291	1.024509	7.312097
C	-1.141524	-0.739168	8.915138
C	-2.345357	-0.405610	9.532398
C	-2.705904	1.328002	7.908276
H	-0.567706	-1.574199	9.295221
H	-2.673305	-0.973668	10.395464
H	-3.313529	2.123627	7.492827
H	-4.072950	0.882118	9.507544
S	-0.883109	1.995124	-5.941517
S	-0.883109	1.995124	5.941517
C	1.605400	-0.994064	-7.921171
H	1.383670	-0.852920	-8.977927
C	1.605400	-0.994064	7.921171
H	1.383670	-0.852920	8.977927
H	1.583484	-2.078298	7.739414
H	1.583484	-2.078298	-7.739414
C	3.000867	-0.428548	-7.647427
H	3.031772	0.634012	-7.897455
H	3.735740	-0.951860	-8.265374
H	3.298129	-0.539607	-6.604042
C	3.000867	-0.428548	7.647427
H	3.031772	0.634012	7.897455
H	3.298129	-0.539607	6.604042
H	3.735740	-0.951860	8.265374

SCF Done: E(RB+HF-LYP) = -2526.09999572 A.U. after 6 cycles
Sum of electronic and zero-point Energies= -2525.479402
Sum of electronic and thermal Energies= -2525.442055
Sum of electronic and thermal Enthalpies= -2525.441111
Sum of electronic and thermal Free Energies= -2525.552248

Structure 2k:

XYZ-Coordinates:

H	-0.017273	4.783795	-0.175465
C	-0.309593	3.741961	-0.244501
H	-2.397255	4.172318	-0.245164
C	-1.639494	3.402270	-0.288746
C	0.358058	1.400984	-0.333097
C	-2.037155	2.043839	-0.369477
C	0.680055	2.750683	-0.279607
C	-1.023177	1.024343	-0.358791
C	-3.419700	1.671504	-0.421962
H	1.714262	3.065128	-0.248150
C	-3.738105	0.327090	-0.409634
H	-4.779662	0.029583	-0.456539
C	-2.751000	-0.664169	-0.374741
H	-3.077543	-1.695125	-0.380208

C	-1.398271	-0.355294	-0.357603
H	3.077543	1.695125	-0.380208
C	2.751000	0.664169	-0.374741
C	1.398271	0.355294	-0.357603
C	3.419700	-1.671504	-0.421962
C	1.023177	-1.024343	-0.358791
C	3.738105	-0.327090	-0.409634
C	2.037155	-2.043839	-0.369477
C	-0.358058	-1.400984	-0.333097
H	4.779662	-0.029583	-0.456539
H	2.397255	-4.172318	-0.245164
C	-0.680055	-2.750683	-0.279607
H	-1.714262	-3.065128	-0.248150
C	0.309593	-3.741961	-0.244501
H	0.017273	-4.783795	-0.175465
C	1.639494	-3.402270	-0.288746
C	4.517576	-2.673119	-0.493172
C	6.695928	-4.489274	-0.664334
C	4.595291	-3.618825	-1.522471
C	5.546197	-2.661607	0.458146
C	6.623898	-3.535703	0.364983
C	5.652678	-4.519577	-1.598777
H	3.821797	-3.648800	-2.280834
H	5.505023	-1.960414	1.283485
H	5.666233	-5.244446	-2.402056
C	-4.517576	2.673119	-0.493172
C	-6.695928	4.489274	-0.664334
C	-5.546197	2.661607	0.458146
C	-4.595291	3.618825	-1.522471
C	-5.652678	4.519577	-1.598777
C	-6.623898	3.535703	0.364983
H	-5.505023	1.960414	1.283485
H	-3.821797	3.648800	-2.280834
H	-5.666233	5.244446	-2.402056
N	7.793240	-5.379405	-0.715685
N	-7.793240	5.379405	-0.715685
C	8.224670	-5.968212	0.497600
C	9.105585	-7.059388	2.941262
C	8.543909	-7.328360	0.605312
C	8.327826	-5.170625	1.651406
C	8.746631	-5.715799	2.861707
C	8.999959	-7.860745	1.809509
H	8.430908	-7.981022	-0.250377
H	8.801639	-5.079191	3.737218
H	9.254521	-8.913195	1.860518
H	9.450593	-7.473841	3.880920
C	-8.224670	5.968212	0.497600
C	-9.105585	7.059388	2.941262
C	-8.327826	5.170625	1.651406
C	-8.543909	7.328360	0.605312
C	-8.999959	7.860745	1.809509
C	-8.746631	5.715799	2.861707
H	-8.430908	7.981022	-0.250377
H	-9.254521	8.913195	1.860518
H	-8.801639	5.079191	3.737218
H	-9.450593	7.473841	3.880920
S	7.977755	-3.426158	1.521142
S	-7.977755	3.426158	1.521142
C	8.140826	-6.019194	-1.987857
H	8.995663	-6.664154	-1.790550
H	7.333228	-6.672555	-2.348058
C	-8.140826	6.019194	-1.987857

```
 H    -8.995663     6.664154    -1.790550
 H    -7.333228     6.672555    -2.348058
 C    -8.543909     5.011188    -3.066608
 H    -9.395287     4.417457    -2.727266
 H    -7.734322     4.326335    -3.321119
 H    -8.833812     5.544582    -3.976118
 C     8.543909    -5.011188    -3.066608
 H     9.395287    -4.417457    -2.727266
 H     7.734322    -4.326335    -3.321119
 H     8.833812    -5.544582    -3.976118

SCF Done:  E(RB+HF-LYP) =  -2756.02633429     A.U. after   10 cycles
Sum of electronic and zero-point Energies=          -2755.345980
Sum of electronic and thermal Energies=             -2755.305248
Sum of electronic and thermal Enthalpies=           -2755.304304
Sum of electronic and thermal Free Energies=        -2755.421969
```

Structure 2l:

XYZ-Coordinates:

```
 N    -0.000134     0.659220    -0.092438
 C     0.008776    -0.686950     2.292872
 C    -0.006075     1.356490     1.055919
 N     0.000134    -0.659220    -0.092438
 C     0.006075    -1.356490     1.055919
 C    -0.008776     0.686950     2.292872
 H    -0.028945     1.234318     3.226607
 H     0.028945    -1.234318     3.226607
 C    -0.019360     2.829325     0.930852
 C    -0.084425     5.668506     0.633451
 C    -0.292532     3.427803    -0.308739
 C     0.244505     3.679115     2.007486
 C     0.199597     5.061531     1.867399
 C    -0.297522     4.804849    -0.462474
 H    -0.472366     2.789342    -1.163698
 H     0.496118     3.277740     2.981512
 H     0.397207     5.664979     2.740151
 C     0.019360    -2.829325     0.930852
 C     0.084425    -5.668506     0.633451
 C    -0.244505    -3.679115     2.007486
 C     0.292532    -3.427803    -0.308739
 C     0.297522    -4.804849    -0.462474
 C    -0.199597    -5.061531     1.867399
 H    -0.496118    -3.277740     2.981512
 H     0.472366    -2.789342    -1.163698
 N    -0.131823     7.067494     0.485495
 N     0.131823    -7.067494     0.485495
 H    -0.397207    -5.664979     2.740151
 C     0.419600     7.907223     1.556192
 H     0.734186     8.845959     1.096026
 H     1.333696     7.422786     1.906001
 C    -0.419600    -7.907223     1.556192
 H    -1.333696    -7.422786     1.906001
 H    -0.734186    -8.845959     1.096026
 C    -0.912580     7.684752    -0.521513
 C    -2.481728     8.909837    -2.535213
 C    -1.194587     7.022617    -1.732073
 C    -1.424369     8.982371    -0.364141
```

```
C    -2.182901     9.590350    -1.362447
C    -1.990440     7.618500    -2.706480
H    -1.233874     9.538213     0.541380
H    -2.549016    10.598235    -1.204348
H    -2.203066     7.067297    -3.615425
H    -3.084603     9.370675    -3.308211
C     0.912580    -7.684752    -0.521513
C     2.481728    -8.909837    -2.535213
C     1.424369    -8.982371    -0.364141
C     1.194587    -7.022617    -1.732073
C     1.990440    -7.618500    -2.706480
C     2.182901    -9.590350    -1.362447
H     1.233874    -9.538213     0.541380
H     2.203066    -7.067297    -3.615425
H     2.549016   -10.598235    -1.204348
H     3.084603    -9.370675    -3.308211
S    -0.419600     5.467462    -2.108799
S     0.419600    -5.467462    -2.108799
C    -0.505213     8.197437     2.750112
H    -1.419383     8.708872     2.446666
H     0.018597     8.837640     3.466084
H    -0.804284     7.286230     3.269416
C     0.505213    -8.197437     2.750112
H    -0.018597    -8.837640     3.466084
H     0.804284    -7.286230     3.269416
H     1.419383    -8.708872     2.446666

SCF Done:  E(RB+HF-LYP) =  -2250.81684651     A.U. after    8 cycles
Sum of electronic and zero-point Energies=          -2250.312825
Sum of electronic and thermal Energies=             -2250.281336
Sum of electronic and thermal Enthalpies=           -2250.280392
Sum of electronic and thermal Free Energies=        -2250.377976
```

Structure 2m:

XYZ-Coordinates:

```
C     0.017798     0.708678    -1.591883
H     0.012630     1.304575    -2.495246
C     0.031795     1.265046    -0.335578
C    -0.017798    -0.708678    -1.591883
H    -0.012630    -1.304575    -2.495246
C    -0.031795    -1.265046    -0.335578
S     0.000000     0.000000     0.876376
C     0.071645     2.680620     0.040365
C     0.158631     5.435985     0.732653
C     0.699332     3.619448    -0.794694
C    -0.519325     3.154497     1.219231
C    -0.488901     4.503357     1.552117
C     0.755350     4.962590    -0.449911
H     1.182664     3.291429    -1.707098
H    -1.041881     2.465688     1.872797
H    -0.983833     4.829355     2.457395
C    -0.071645    -2.680620     0.040365
C    -0.158631    -5.435985     0.732653
C     0.519325    -3.154497     1.219231
C    -0.699332    -3.619448    -0.794694
C    -0.755350    -4.962590    -0.449911
C     0.488901    -4.503357     1.552117
```

```
 H     1.041881    -2.465688     1.872797
 H    -1.182664    -3.291429    -1.707098
 H     0.983833    -4.829355     2.457395
 N     0.222761     6.811698     1.045921
 N    -0.222761    -6.811698     1.045921
 C     0.000000     7.741435     0.001404
 C    -0.375282     9.559184    -2.118066
 C     0.594727     7.522148    -1.254131
 C    -0.808449     8.874830     0.159668
 C    -0.975213     9.783244    -0.883539
 C     0.393236     8.412471    -2.304935
 H    -1.319623     9.049473     1.097347
 H    -1.594720    10.659226    -0.728896
 H     0.851984     8.208620    -3.265585
 H    -0.511919    10.259267    -2.933526
 C     0.000000    -7.741435     0.001404
 C     0.375282    -9.559184    -2.118066
 C     0.808449    -8.874830     0.159668
 C    -0.594727    -7.522148    -1.254131
 C    -0.393236    -8.412471    -2.304935
 C     0.975213    -9.783244    -0.883539
 H     1.319623    -9.049473     1.097347
 H    -0.851984    -8.208620    -3.265585
 H     1.594720   -10.659226    -0.728896
 H     0.511919   -10.259267    -2.933526
 S    -1.672250    -6.114768    -1.458045
 S     1.672250     6.114768    -1.458045
 C     0.055190     7.239806     2.438075
 H     0.124538     8.326407     2.442399
 H    -0.943854     6.988652     2.821933
 C    -0.055190    -7.239806     2.438075
 H     0.943854    -6.988652     2.821933
 H    -0.124538    -8.326407     2.442399
 C     1.144212     6.689208     3.361882
 H     0.993930     7.074164     4.374298
 H     2.129195     7.006685     3.013446
 H     1.137836     5.599815     3.411055
 C    -1.144212    -6.689208     3.361882
 H    -1.137836    -5.599815     3.411055
 H    -0.993930    -7.074164     4.374298
 H    -2.129195    -7.006685     3.013446

SCF Done:  E(RB+HF-LYP) =  -2539.53177620     A.U. after    7 cycles
Sum of electronic and zero-point Energies=          -2539.037475
Sum of electronic and thermal Energies=             -2539.005946
Sum of electronic and thermal Enthalpies=           -2539.005002
Sum of electronic and thermal Free Energies=        -2539.102139
```

Structure 2n:

XYZ-Coordinates:

```
 C     1.448239    -0.145560    -1.246951
 H     2.340614    -0.276343    -0.648106
 C     0.193047    -0.013102    -0.695381
 C     1.459812    -0.115841    -2.661601
 H     2.358744    -0.239389    -3.250603
 C     0.216320     0.041923    -3.225793
 S    -0.999987     0.170671    -1.969005
 C    -1.454589     0.107460     1.244835
```

H	-2.349080	0.219191	0.645990
C	-0.197281	-0.008066	0.695381
C	-1.464046	0.081973	2.659485
H	-2.365094	0.192821	3.248487
C	-0.218436	-0.054623	3.225793
S	0.999987	-0.166437	1.969005
C	0.142885	-0.117311	4.642055
C	0.804989	-0.242882	7.404558
C	1.398550	0.293372	5.110194
C	-0.782788	-0.582993	5.591049
C	-0.454672	-0.659119	6.936719
C	1.719574	0.243151	6.461268
H	2.128289	0.690292	4.415049
H	-1.758033	-0.927255	5.269638
H	2.690439	0.597154	6.780272
C	-0.145001	0.113077	-4.642055
C	-0.804989	0.253466	-7.404558
C	-1.404900	-0.282788	-5.112310
C	0.784904	0.574527	-5.588933
C	0.458906	0.657003	-6.934603
C	-1.723808	-0.226217	-6.463384
H	-2.138873	-0.675476	-4.417165
H	1.764383	0.908205	-5.267522
H	-2.698905	-0.569636	-6.784506
N	1.098784	-0.318721	8.783250
N	-1.096668	0.335655	-8.783250
C	-2.495982	0.393421	-9.218341
H	-2.484622	0.427408	-10.306560
C	2.498098	-0.365903	9.218341
H	2.488856	-0.397774	10.306560
C	0.097668	0.081633	9.700712
C	-1.946609	0.821745	11.493008
C	0.374320	0.881463	10.817102
C	-1.234419	-0.317038	9.485391
C	-2.245027	0.065084	10.362690
C	-0.635422	1.228646	11.713306
H	1.378417	1.246300	10.987099
H	-3.264242	-0.245378	10.160952
H	-0.390398	1.836936	12.576270
H	-2.733989	1.099813	12.183614
C	-0.097668	-0.073167	-9.700712
C	1.940259	-0.828095	-11.493008
C	-0.380670	-0.868763	-10.819218
C	1.236535	0.312804	-9.483275
C	2.245027	-0.075668	-10.360574
C	0.624838	-1.222296	-11.715422
H	-1.389001	-1.223016	-10.991333
H	3.266358	0.224210	-10.158836
H	0.375582	-1.826352	-12.580504
H	2.725523	-1.110397	-12.183614
S	1.607444	1.372187	-8.096862
S	-1.596860	-1.382771	8.101096
H	3.040656	0.548452	8.937684
H	-3.044890	-0.516702	-8.939800
C	3.233428	-1.607854	8.709196
H	2.727299	-2.512001	9.054179
H	4.255460	-1.613534	9.097860
H	3.286297	-1.644678	7.620487
C	-3.220728	1.641722	-8.709196
H	-3.273597	1.676428	-7.620487
H	-4.242760	1.655868	-9.097860
H	-2.706131	2.541635	-9.052063

```
SCF Done:  E(RB+HF-LYP) =  -3091.40629091     A.U. after    1 cycles
Sum of electronic and zero-point Energies=          -3090.865219
Sum of electronic and thermal Energies=             -3090.829978
Sum of electronic and thermal Enthalpies=           -3090.829033
Sum of electronic and thermal Free Energies=        -3090.935099
```

Structure 2o:

XYZ-Coordinates:

```
 H     2.444955     3.483170     1.246599
 C     1.755731     2.840678     0.710288
 H     0.905486     2.034226     2.482180
 C     0.896812     2.032863     1.400139
 C     0.896812     2.032863    -1.400139
 C    -0.023349     1.170307     0.722487
 C     1.755731     2.840678    -0.710288
 C    -0.023349     1.170307    -0.722487
 C    -0.910160     0.330729     1.425861
 H     2.444955     3.483170    -1.246599
 H     0.905486     2.034226    -2.482180
 C    -1.794274    -0.511650     0.722382
 C    -2.710910    -1.378083     1.399847
 C    -1.794274    -0.511650    -0.722382
 H    -2.717298    -1.381725    -2.481930
 C    -0.910160     0.330729    -1.425861
 C    -3.565648    -2.190595     0.710284
 H    -2.717298    -1.381725     2.481930
 H    -4.249052    -2.839264     1.246682
 C    -3.565648    -2.190595    -0.710284
 H    -4.249052    -2.839264    -1.246682
 C    -2.710910    -1.378083    -1.399847
 C    -0.914085     0.334287    -2.922410
 C    -0.936750     0.323511    -5.756448
 C    -0.137555    -0.579173    -3.642915
 C    -1.683614     1.251963    -3.641109
 C    -1.683274     1.260578    -5.033762
 C    -0.164075    -0.599186    -5.034186
 H     0.484699    -1.291886    -3.114075
 H    -2.283664     1.979119    -3.106294
 H    -2.273757     2.003392    -5.553781
 C    -0.914085     0.334287     2.922410
 C    -0.936750     0.323511     5.756448
 C    -0.137555    -0.579173     3.642915
 C    -1.683614     1.251963     3.641109
 C    -1.683274     1.260578     5.033762
 C    -0.164075    -0.599186     5.034186
 H     0.484699    -1.291886     3.114075
 H    -2.283664     1.979119     3.106294
 H    -2.273757     2.003392     5.553781
 N    -0.922910     0.296285    -7.175020
 N    -0.922910     0.296285     7.175020
 C     0.310585     0.114470    -7.824128
 C     2.793601    -0.323426    -9.089981
 C     1.226926    -0.831221    -7.317894
 C     0.680468     0.845996    -8.963887
 C     1.892804     0.618691    -9.599653
 C     2.455758    -1.032795    -7.927850
 H     0.022939     1.609512    -9.356690
```

H	2.153534	1.186772	-10.483682
H	3.149210	-1.755015	-7.515505
C	0.310585	0.114470	7.824128
C	2.793601	-0.323426	9.089981
C	1.226926	-0.831221	7.317894
C	0.680468	0.845996	8.963887
C	1.892804	0.618691	9.599653
C	2.455758	-1.032795	7.927850
H	0.022939	1.609512	9.356690
H	2.153534	1.186772	10.483682
H	3.149210	-1.755015	7.515505
S	0.742129	-1.844020	-5.934235
S	0.742129	-1.844020	5.934235
C	-2.054632	0.871144	-7.913512
H	-1.834399	0.748525	-8.972548
C	-2.054632	0.871144	7.913512
H	-1.834399	0.748525	8.972548
H	-2.145134	1.951086	7.734218
H	-2.145134	1.951086	-7.734218
C	-3.375222	0.157556	-7.616622
H	-3.294116	-0.903223	-7.862510
H	-4.170168	0.594412	-8.226818
H	-3.668761	0.242108	-6.569902
C	-3.375222	0.157556	7.616622
H	-3.294116	-0.903223	7.862510
H	-3.668761	0.242108	6.569902
H	-4.170168	0.594412	8.226818
C	4.046936	-0.552592	-9.734989
N	5.060769	-0.736455	-10.258603
C	4.046936	-0.552592	9.734989
N	5.060769	-0.736455	10.258603

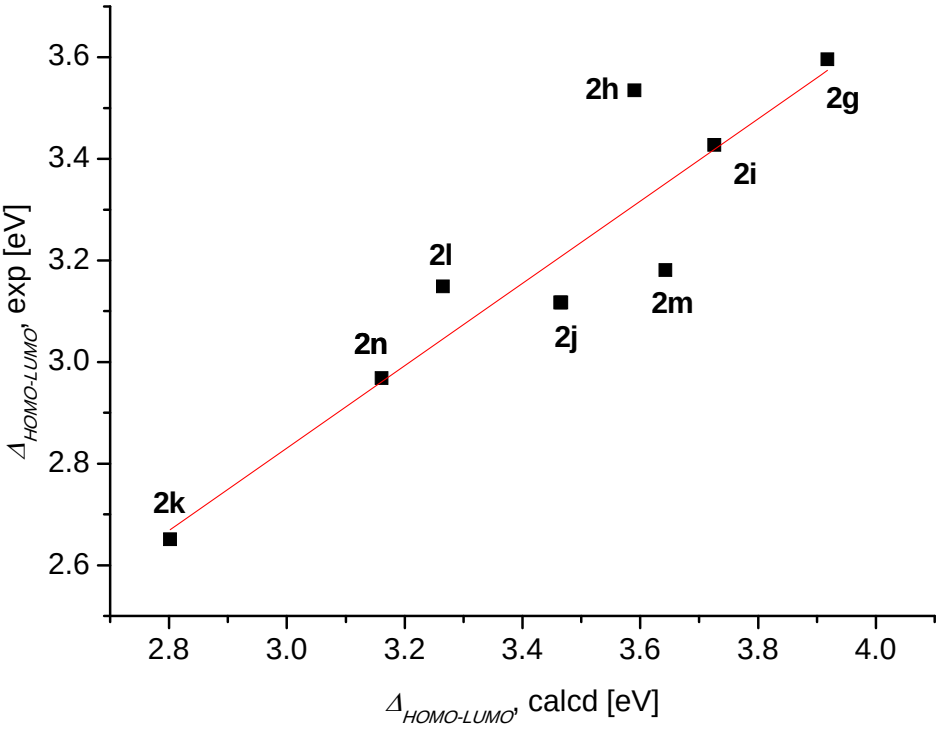
SCF Done: E(RB+HF-LYP) = -2710.63106359 A.U. after 1 cycles
Sum of electronic and zero-point Energies= -2710.012984
Sum of electronic and thermal Energies= -2709.971966
Sum of electronic and thermal Enthalpies= -2709.971022
Sum of electronic and thermal Free Energies= -2710.090776

6. Correlation of UV/Vis λ_{max} and computed $\Delta_{HOMO-LUMO}$ energies

Structure	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
2g	-6.101	-5.351	-5.163	-1.245	-0.588	-0.575
2h	-5.924	-5.118	-5.03	-1.44	-0.875	-0.61
2i	-5.807	-5.3	-5.167	-1.441	-0.694	-0.644
2j	-5.337	-5.329	-5.328	-1.862	-0.783	-0.656
2k	-5.458	-5.316	-4.979	-2.177	-0.879	-0.808
2l	-6.128	-5.203	-5.029	-1.764	-1.469	-0.774
2m	-5.896	-5.371	-5.111	-1.468	-0.633	-0.632
2n	-5.68	-5.359	-5.013	-1.852	-0.959	-0.667
2o	-5.824	-5.809	-5.615	-2.151	-1.568	-1.564

Energies in [eV]

Compound/Structure	$\Delta_{HOMO-LUMO}$, calcd [eV]	λ_{max}, exp [nm]	$\Delta_{HOMO-LUMO}$, exp [eV]
2g	3.918	345	3.596
2h	3.590	351	3.535
2i	3.726	362	3.427
2j	3.466	398	3.117
2k	2.802	468	2.651
2l	3.265	394	3.149
2m	3.643	390	3.181
2n	3.161	418	2.968
2o	3.464	398	3.117



Linear regression analysis: $\Delta_{HOMO-LUMO,exp} = 0.81 \cdot \Delta_{HOMO-LUMO,exp} + 0.40$ [eV]; $r^2 = 0.82156$.