Towards Interlocked Structures

based on H-bonded barbiturate complexes

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APPENDIX 1

XRD data

General considerations

The crystals of receptors **17** (with acetone, with DCM) and **18**, and of the complexes of **18** with barbital and **39**, have been obtained and analysed in the University Bordeaux 1 by N. D. McClenaghan, B. Kauffmann and J.-P. Desvergnes. The structures have been solved using *superflip*[1] and refined with *SHELXL*.[2] Full-matrix least-squares refinement was performed on F^2 for all unique reflections, minimizing $w(F_o^2 - F_c^2)^2$, with anisotropic displacement parameters for non-hydrogen atoms. The positions of the hydrogen atoms were located on a subsequent differential electron-density map. Hydrogen atoms were mostly spotted in Fourier differences but included in idealized positions and refined with a riding model, with U_{iso} constrained to 1.2 U_{eq} value of the parent atom (1.5 U_{eq} when CH_3). The positions and the isotropic displacement parameters of the remaining hydrogen atoms were refined freely.

The crystals of **38**, **39** and **42** have been obtained in Birmingham and analysed by L. Malle. More details are given for each crystal structure.

[1] Palatinus, L. & Chapuis, G. (2007). *Superflip*. http://superspace.epfl.ch/superflip .
[2] G. M. Sheldrick, *Acta Cryst.*, 2008, A**64**, 112–122

Crystal structures

17•acetone

The crystals belong to the monoclinic P $2_1/c$ space group with unit cell parameters a = 14.4835(12) Å, b = 9.3830(8) Å, c = 25.805(2) Å, α = 90.00°, β = 93.91(4)°, γ = 90.00°. Mr = 656.81, V = 3498.61 $Å^3$, ρ_{calc} = 1.247 $g.cm^{-3}$, Z = 4, Z' = 0.

As can be seen in **Figures A1.1** and **A1.2**, the crystal contains one equivalent of acetone, which forms an inclusion complex with the receptor.

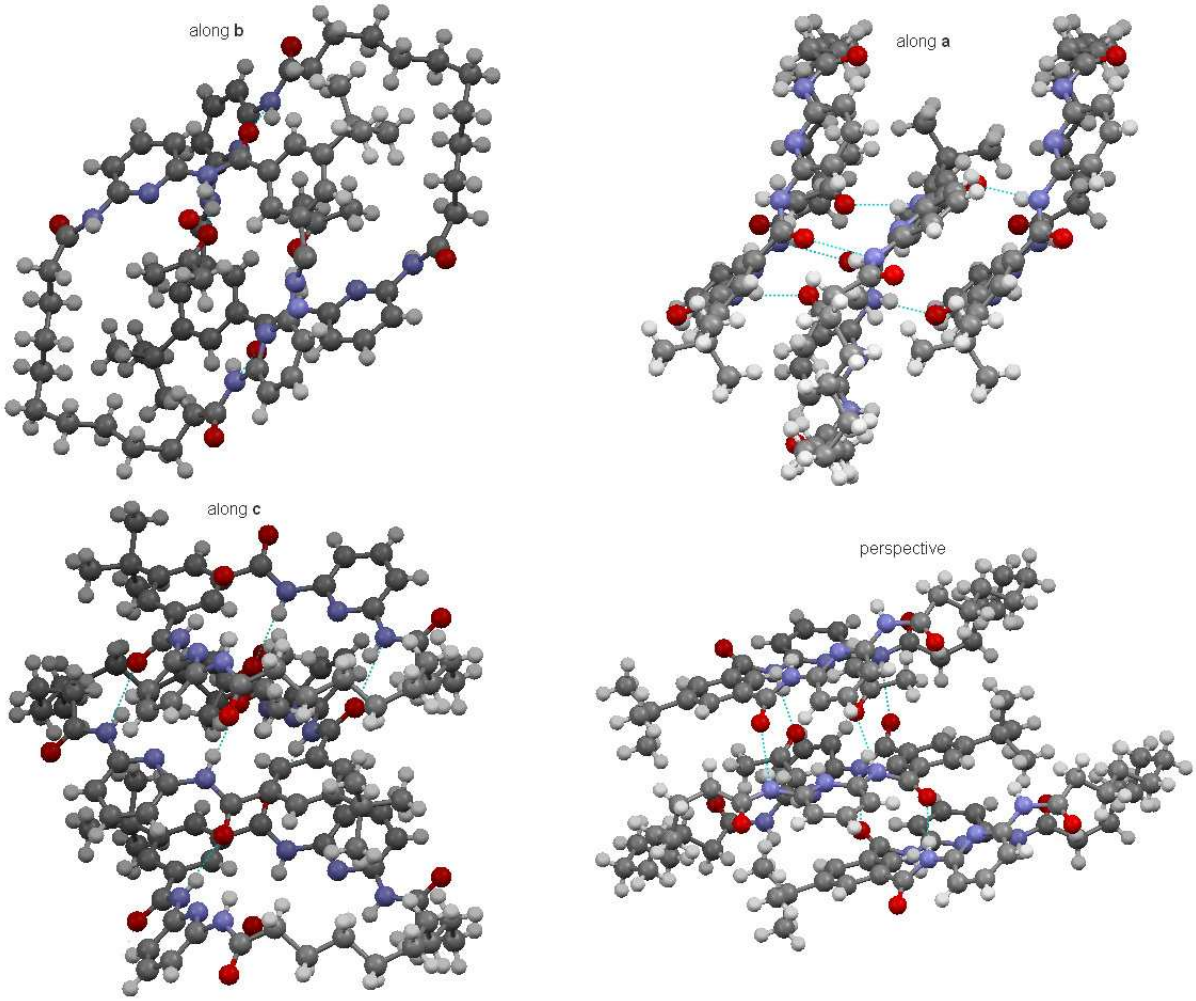


Figure A1-1. Partial X-ray structure of **17•acetone** along three axes and in perspectivre, highlighting inter-ring interactions.

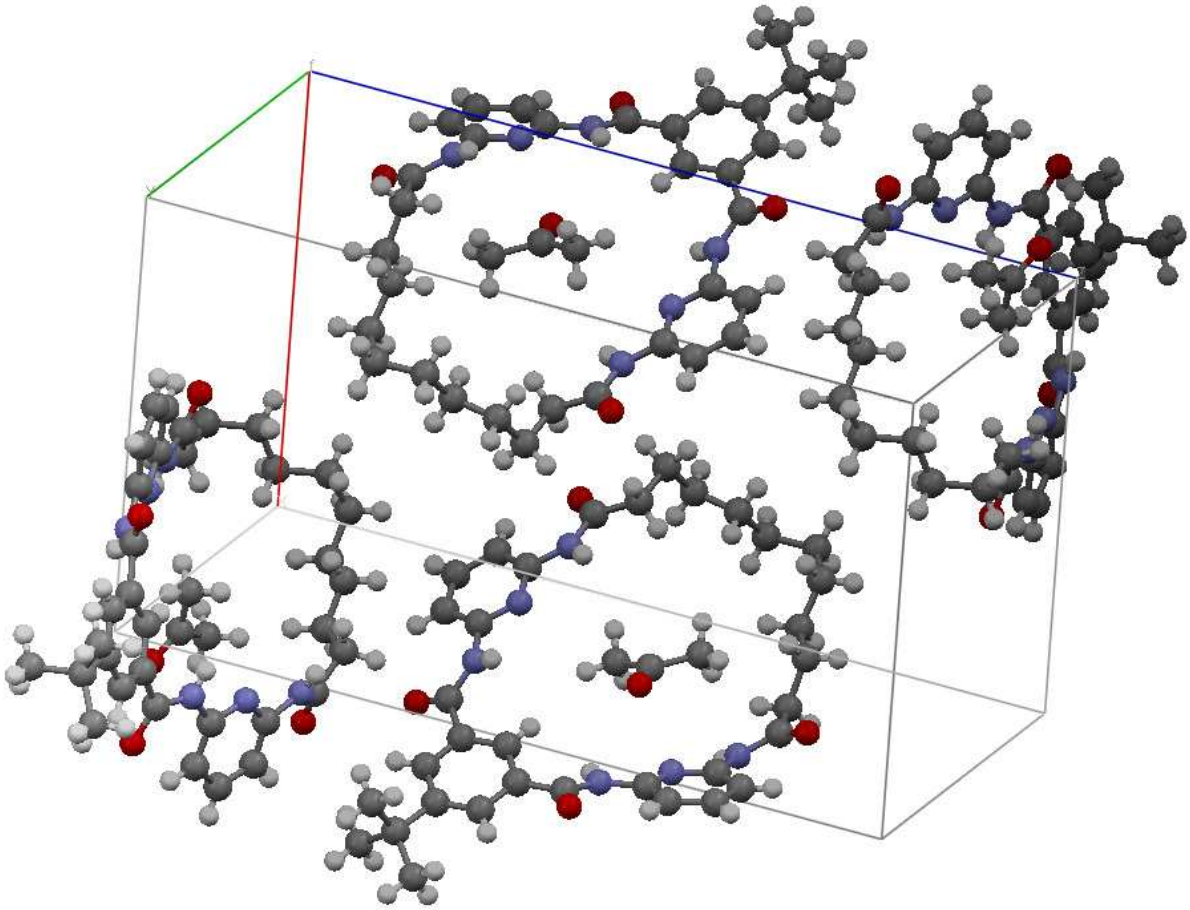


Figure A1-2. X-ray structure of **17•acetone** in perspective

17•dichloromethane

The crystals belong to the monoclinic P $2_1/c$ space group with unit cell parameters a = 14.538 Å, b = 9.322 Å, c = 25.786 Å, α = 90.00°, β = 94.68°, γ = 90.00°. Mr = 683.67, V = 3482.95 $Å^3$, ρ_{calc} = 1.304g.cm^{-3}, Z = 1, Z' = 0.

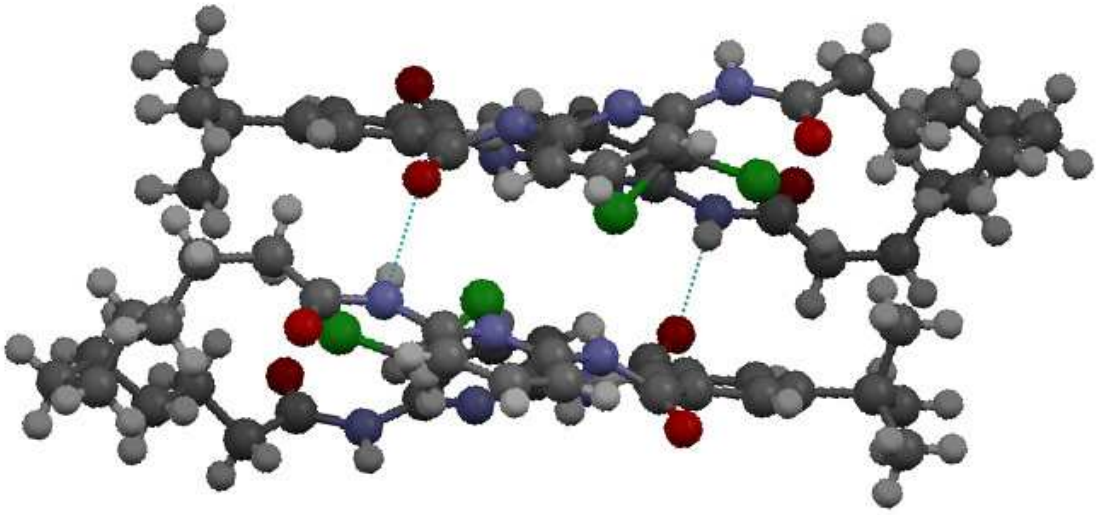


Figure A1-3. Partial crystal structure of **17•DCM**, showing inter-ring H-bonds.

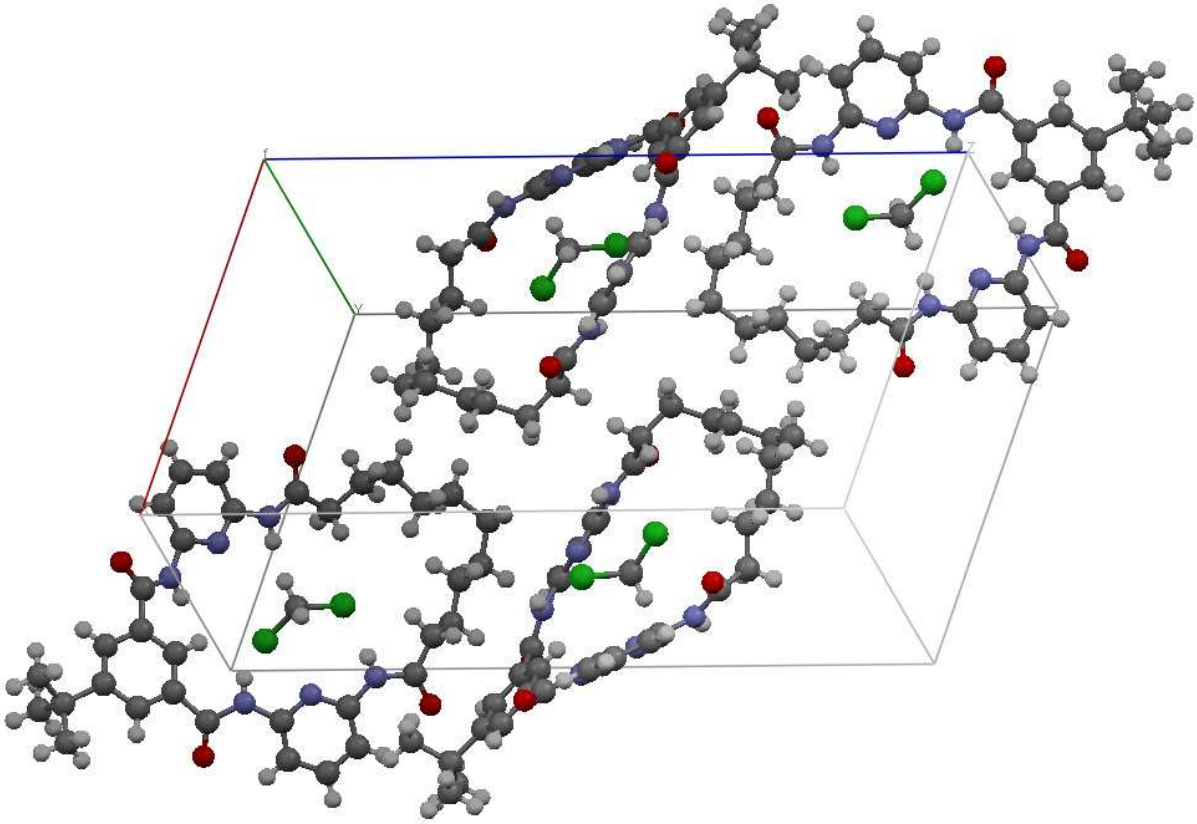


Figure A1-4. Crystal structure of **17•DCM** in perspective.

18

The crystals belong to the triclinic P-1 space group with unit cell parameters a = 9.857(2) Å, b = 18.884(4) Å, c = 19.610(4) Å, $\alpha = 93.02(3)°$, $\beta = 93.39(3)°$, $\gamma = 90.21(3)°$. Mr = 654.84, V = 3638(8) $Å^3$, $\rho_{calc} = 1.195$ $g.cm^{-3}$, Z = 4, $\mu = 0.627$ mm^{-1}, no absorption correction, Ω scans, 37510 reflections collected, $\theta_{max} = 61.16°$, 10698 independent with $I > 2\sigma(I)$ (Rint = 0.119).

Refinement statistics : 866 parameters, 4 restraints, Goodness-of-fit on $F^2 = 1.32$, Final R indices $[I > 2\sigma(I)]$, R1 = 0.1473, wR2 = 0.3701, R indices (all data) R1 = 0.2012, wR2 = 0.4315.

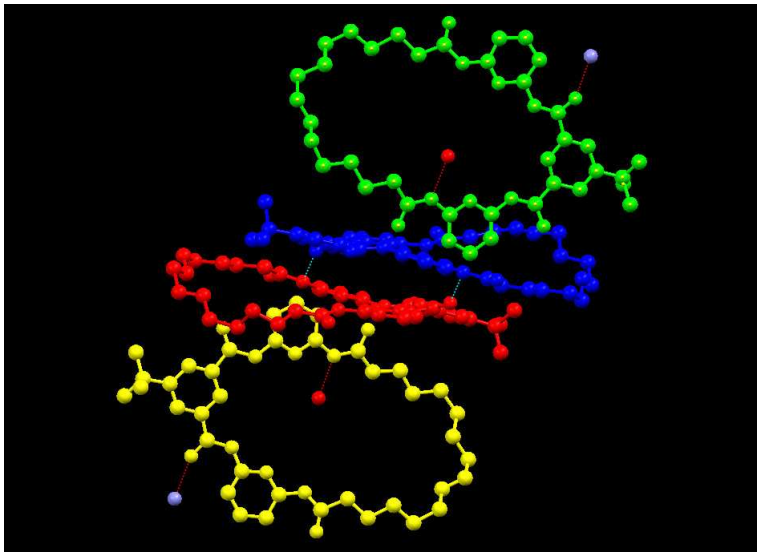


Figure A1-5. X-ray structure of **18** highlighting inter-ring interactions.

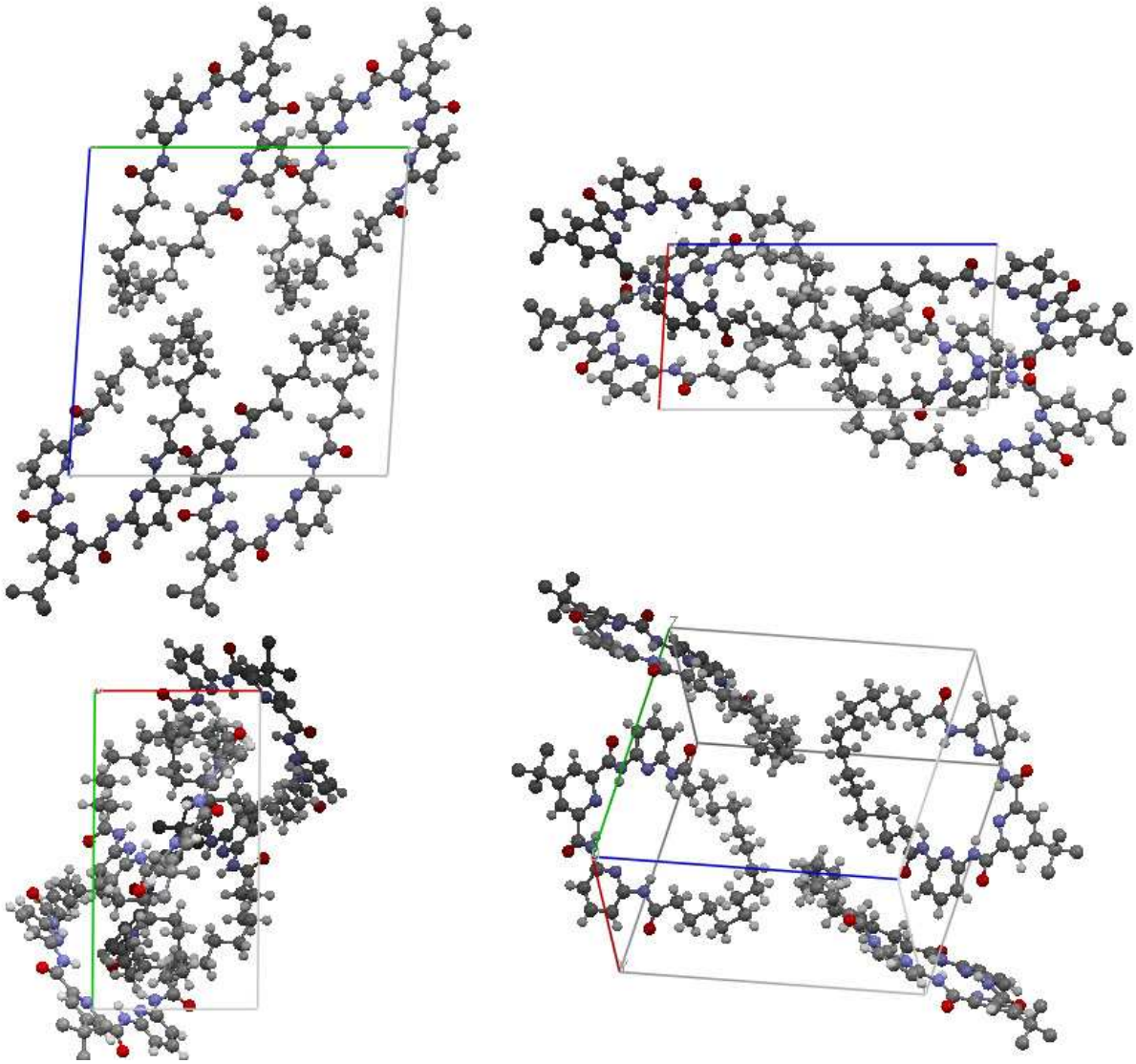


Figure A1-6. X-ray structure of **18**, along three axes and in perspective

18•barbital

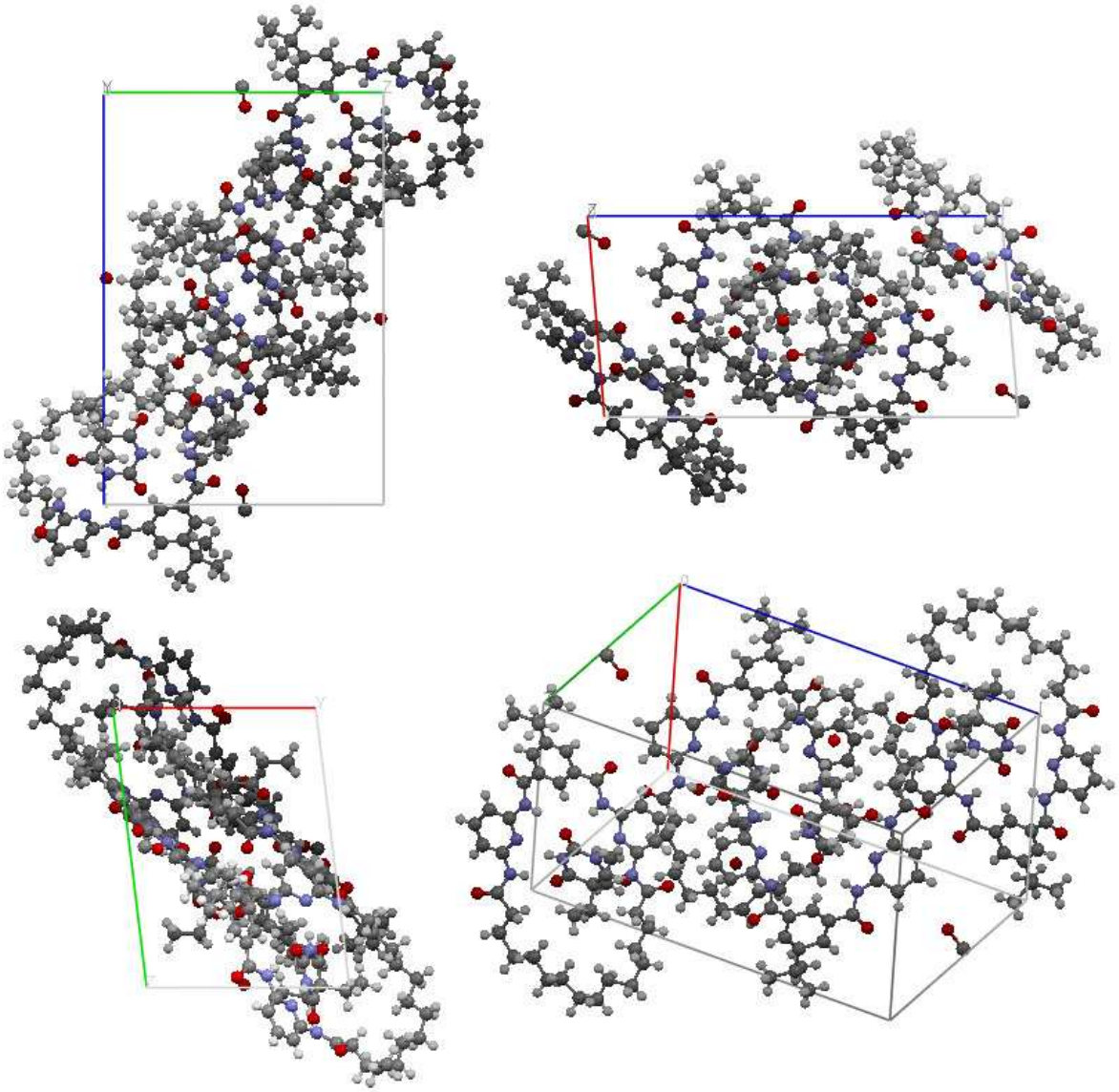


Figure A1-7. X-ray structure of **18•barbital** complex along three axes and in perspective.

The crystals belong to the triclinic P-1 space group with unit cell parameters a = 12.036(2) Å, b = 16.670(3) Å, c = 24.484(5) Å, α = 89.40(3)°, β = 85.20(3)°, γ = 83.07(3)°. Mr = 871.77, V = 4859(17) $Å^3$, ρ_{calc} = 1.192 $g.cm^{-3}$, Z = 4, μ = 0.906 mm^{-1}, no absorption correction, Ω scans, 38369 reflections collected, θ_{max} = 38.07°, 5188 independent with I > 2σ(I) (Rint = 0.171).

Refinement statistics : 1048 parameters, 125 restraints, Goodness-of-fit on F^2 = 1.41, Final R indices [I > 2σ(I)], R1 = 0.1708, wR2 = 0.2307, R indices (all data) R1 = 0.3855, wR2 = 0.4174

It should be mentioned here that the crystals of the complex, unlike the individual components, were of not of very high quality, making it difficult to find a suitable single crystal. A very small crystal was used, which was far to be single. The best data set was

obtained by integrating the data with the twinsolve module of the CrystalClear suite (Rigaku Corporation, © 1997-2002).

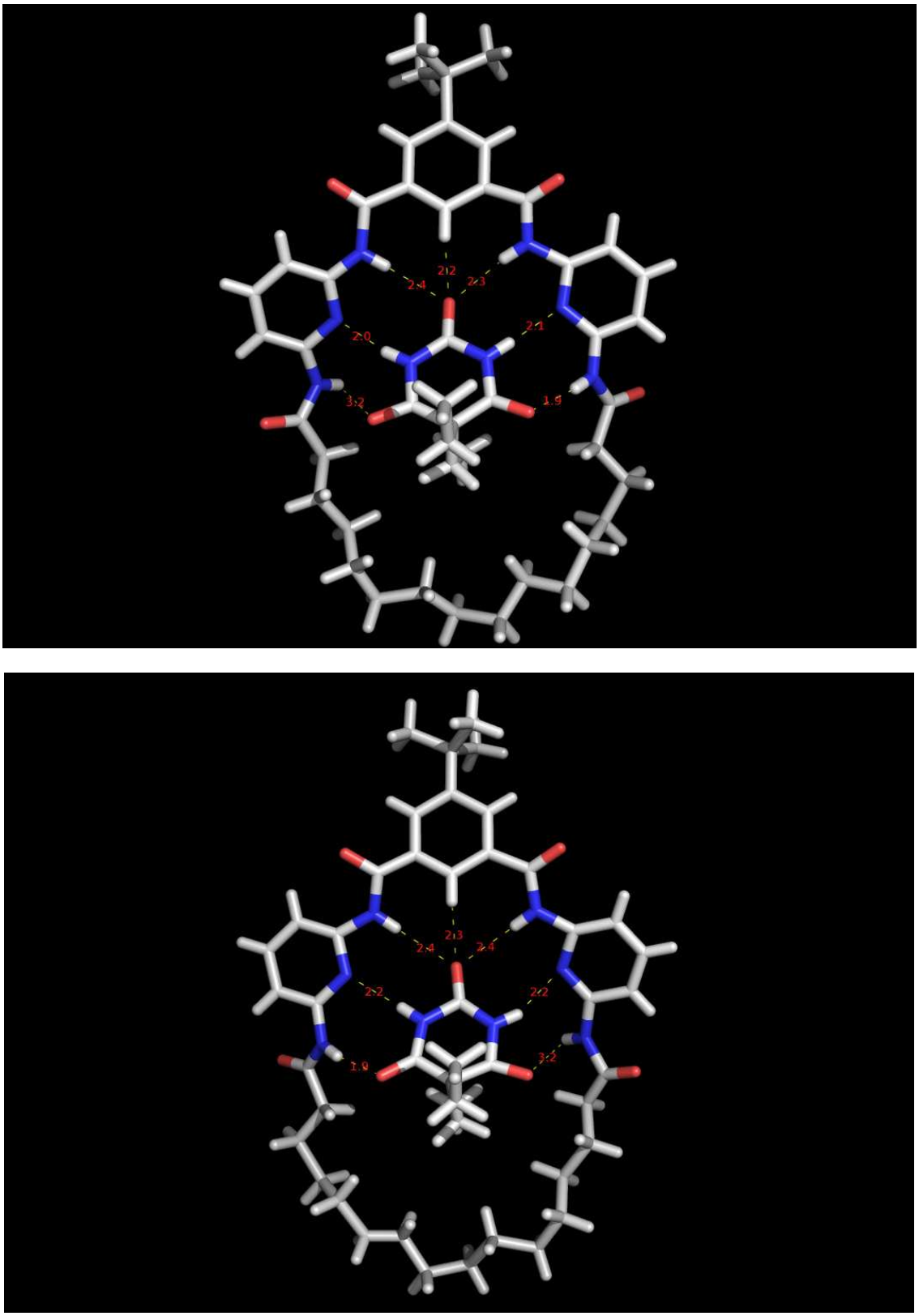


Figure A1-8. Two independent **18•barbital** complexes observed in the unit cell. Disordered water has been omitted.

The planar angles have been measured on both independent **18•barbital** complexes present in the unit cell. The whole receptor molecule and the ring of the barbital have been used to calculate the tilting angle using Mercury (shown in **Figure A1-5**). Angles of 24.31° and 26.65° have been measured.

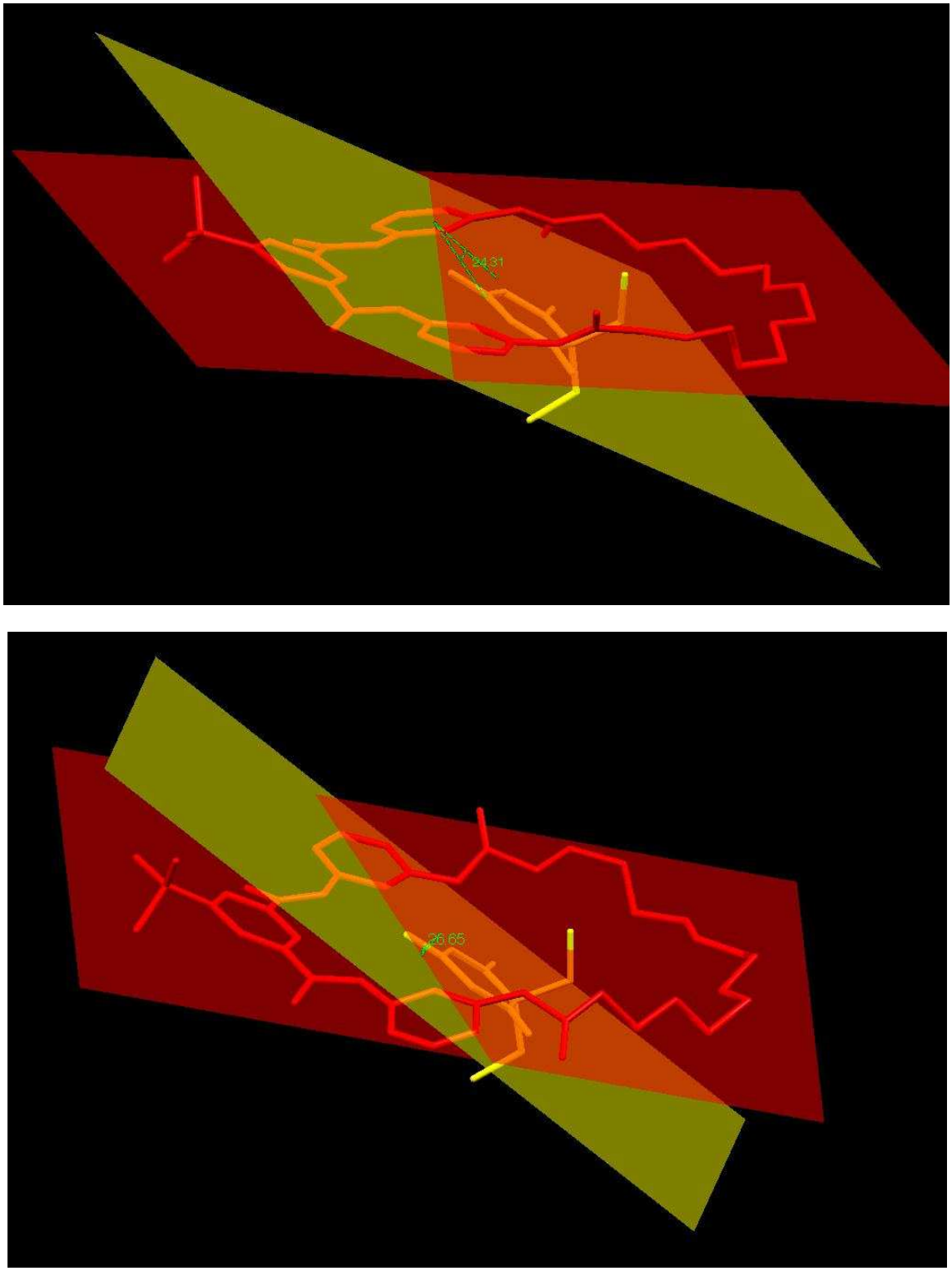


Figure A1-9. X-ray structure of the two independent **18•barbital** complexes showing molecular planes with intermolecular angles tilting with angles of 24.3° and 26.7°.

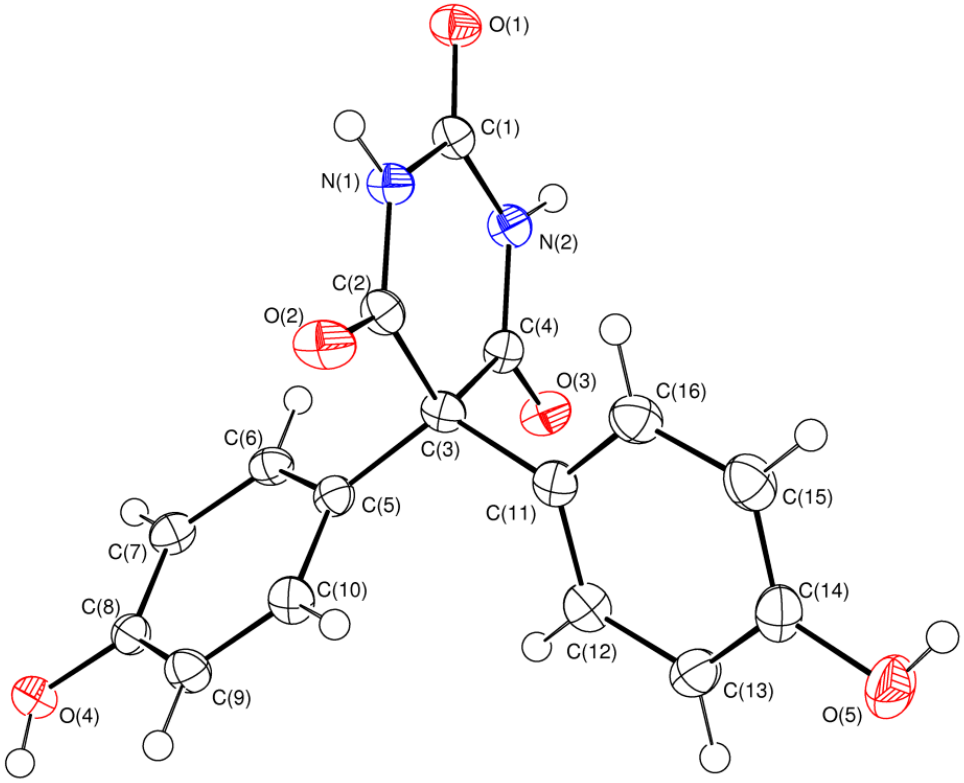


Figure A1-10. X-ray structure of **38**, centered on a single molecule.

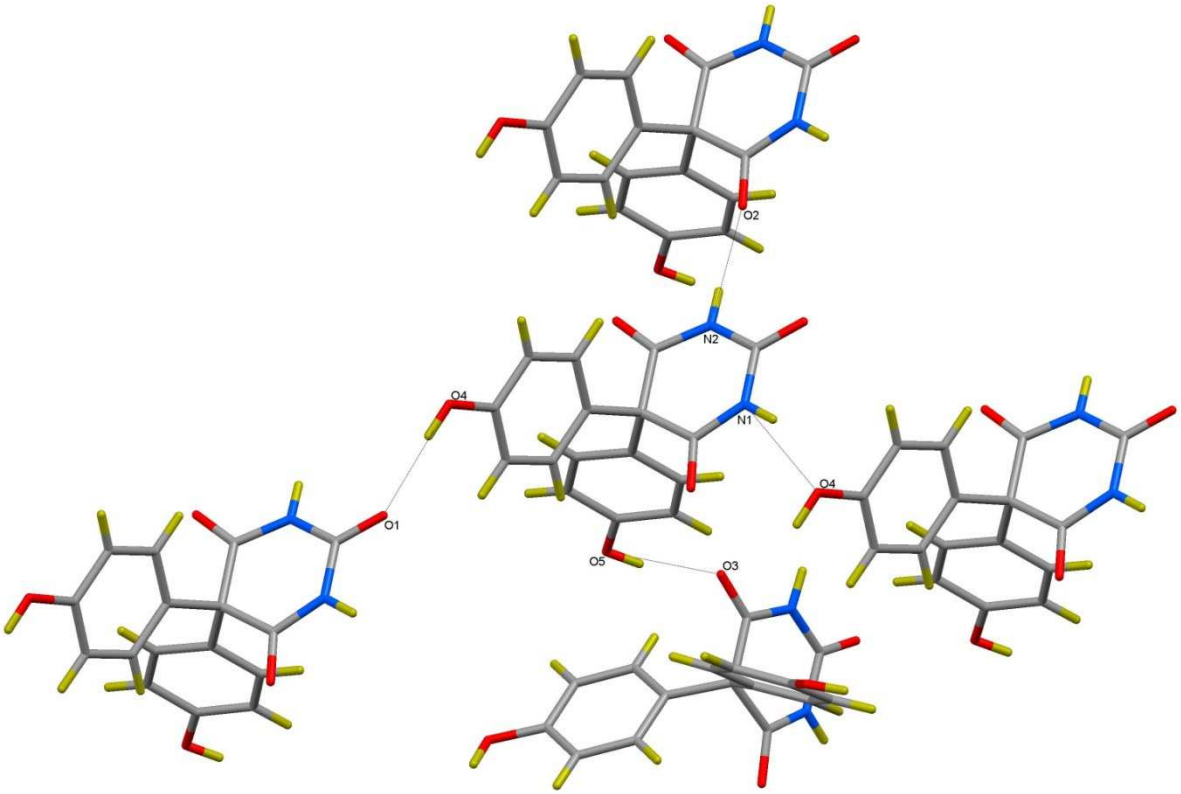


Figure A1-11. X-ray structure of **38** showing intermolecular interactions.

Table A1-1. Crystal data and structure refinement.

Empirical formula	$C_{16}\ H_{12}\ N_2\ O_5$	
Formula weight	312.28	
Temperature	120(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P $na2_1$	
Unit cell dimensions	a = 26.0567(2) Å	α= 90°.
	b = 8.49520(10) Å	β= 90°.
	c = 6.70030(10) Å	γ = 90°.
Volume	1483.16(3) $Å^3$	
Z	4	
Density (calculated)	1.398 Mg/m^3	
Absorption coefficient	0.893 mm^{-1}	
F(000)	648	
Crystal size	0.28 x 0.12 x 0.09 mm^3	
Theta range for data collection	6.80 to 66.59°.	
Index ranges	-30<=h<=27, -9<=k<=10, -7<=l<=7	
Reflections collected	7861	
Independent reflections	1408 [R(int) = 0.0250]	
Completeness to theta = 66.59°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9239 and 0.7880	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1408 / 1 / 210	
Goodness-of-fit on F^2	1.135	
Final R indices [I>2sigma(I)]	R1 = 0.0266, wR2 = 0.0696	
R indices (all data)	R1 = 0.0270, wR2 = 0.0700	
Absolute structure parameter	?	
Largest diff. peak and hole	0.162 and -0.176 e.$Å^{-3}$	

Notes:
It is not possible to determine the absolute structure from the diffraction data as there are no heavy atoms present in the structure.
The hydrogen atoms were fixed as riding models.
The hydrogen bonding is detailed in Table 6.

Table A1-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4306(1)	4990(2)	9966(3)	19(1)
C(2)	4116(1)	3898(2)	6649(3)	21(1)
C(3)	3784(1)	2590(2)	7543(3)	19(1)
C(4)	3762(1)	2640(2)	9822(3)	19(1)
C(5)	4033(1)	1036(2)	6873(3)	20(1)

Table A1-2 (continuation)

	x	y	z	U(eq)
C(6)	4398(1)	289(2)	8048(3)	21(1)
C(7)	4651(1)	-1047(2)	7373(3)	23(1)
C(8)	4536(1)	-1640(2)	5497(3)	20(1)
C(9)	4176(1)	-911(2)	4302(3)	23(1)
C(10)	3928(1)	430(2)	4981(3)	23(1)
C(11)	3224(1)	2820(2)	6859(3)	21(1)
C(12)	2894(1)	1551(2)	6676(3)	25(1)
C(13)	2384(1)	1771(2)	6163(3)	28(1)
C(14)	2196(1)	3281(2)	5849(3)	28(1)
C(15)	2520(1)	4563(2)	6082(4)	30(1)
C(16)	3031(1)	4327(2)	6572(3)	27(1)
N(1)	4353(1)	4931(2)	7906(3)	20(1)
N(2)	3992(1)	3867(2)	10787(3)	22(1)
O(1)	4530(1)	5978(2)	10945(2)	25(1)
O(2)	4175(1)	4026(2)	4858(2)	29(1)
O(3)	3533(1)	1637(2)	10769(2)	26(1)
O(4)	4793(1)	-2974(2)	4917(2)	24(1)
O(5)	1692(1)	3429(2)	5307(3)	35(1)

Table A1-3. Bond lengths [Å] and angles [°].

C(1)-O(1)	1.215(2)	C(9)-C(10)	1.386(3)
C(1)-N(2)	1.373(2)	C(9)-H(9)	0.9500
C(1)-N(1)	1.386(3)	C(10)-H(10)	0.9500
C(2)-O(2)	1.215(3)	C(11)-C(12)	1.385(3)
C(2)-N(1)	1.364(3)	C(11)-C(16)	1.389(3)
C(2)-C(3)	1.530(3)	C(12)-C(13)	1.386(3)
C(3)-C(4)	1.529(3)	C(12)-H(12)	0.9500
C(3)-C(5)	1.538(3)	C(13)-C(14)	1.389(3)
C(3)-C(11)	1.542(3)	C(13)-H(13)	0.9500
C(4)-O(3)	1.218(2)	C(14)-O(5)	1.367(2)
C(4)-N(2)	1.365(3)	C(14)-C(15)	1.387(3)
C(5)-C(6)	1.387(3)	C(15)-C(16)	1.386(3)
C(5)-C(10)	1.395(3)	C(15)-H(15)	0.9500
C(6)-C(7)	1.388(3)	C(16)-H(16)	0.9500
C(6)-H(6)	0.9500	N(1)-H(1)	0.8800
C(7)-C(8)	1.387(3)	N(2)-H(2)	0.8800
C(7)-H(7)	0.9500	O(4)-H(4)	0.8400
C(8)-O(4)	1.373(2)	O(5)-H(5)	0.8400
C(8)-C(9)	1.380(3)		

O(1)-C(1)-N(2)	123.4(2)	N(1)-C(2)-C(3)	118.76(19)
O(1)-C(1)-N(1)	121.39(19)	C(4)-C(3)-C(2)	113.10(17)
N(2)-C(1)-N(1)	115.21(18)	C(4)-C(3)-C(5)	109.38(17)
O(2)-C(2)-N(1)	119.71(19)	C(2)-C(3)-C(5)	105.74(15)
O(2)-C(2)-C(3)	121.53(19)	C(4)-C(3)-C(11)	104.88(16)

Table A1-3 (continuation)

C(2)-C(3)-C(11)	109.03(16)	C(16)-C(11)-C(3)	120.13(17)
C(5)-C(3)-C(11)	114.91(16)	C(11)-C(12)-C(13)	120.91(18)
O(3)-C(4)-N(2)	120.1(2)	C(11)-C(12)-H(12)	119.5
O(3)-C(4)-C(3)	121.30(19)	C(13)-C(12)-H(12)	119.5
N(2)-C(4)-C(3)	118.54(18)	C(12)-C(13)-C(14)	119.98(19)
C(6)-C(5)-C(10)	118.77(18)	C(12)-C(13)-H(13)	120.0
C(6)-C(5)-C(3)	121.03(18)	C(14)-C(13)-H(13)	120.0
C(10)-C(5)-C(3)	119.95(18)	O(5)-C(14)-C(15)	122.82(18)
C(7)-C(6)-C(5)	120.9(2)	O(5)-C(14)-C(13)	117.57(19)
C(7)-C(6)-H(6)	119.5	C(15)-C(14)-C(13)	119.61(18)
C(5)-C(6)-H(6)	119.5	C(16)-C(15)-C(14)	119.84(19)
C(8)-C(7)-C(6)	119.29(19)	C(16)-C(15)-H(15)	120.1
C(8)-C(7)-H(7)	120.4	C(14)-C(15)-H(15)	120.1
C(6)-C(7)-H(7)	120.4	C(15)-C(16)-C(11)	121.03(19)
O(4)-C(8)-C(9)	122.54(19)	C(15)-C(16)-H(16)	119.5
O(4)-C(8)-C(7)	116.79(18)	C(11)-C(16)-H(16)	119.5
C(9)-C(8)-C(7)	120.67(18)	C(2)-N(1)-C(1)	126.78(18)
C(8)-C(9)-C(10)	119.61(19)	C(2)-N(1)-H(1)	116.6
C(8)-C(9)-H(9)	120.2	C(1)-N(1)-H(1)	116.6
C(10)-C(9)-H(9)	120.2	C(4)-N(2)-C(1)	127.06(19)
C(9)-C(10)-C(5)	120.71(18)	C(4)-N(2)-H(2)	116.5
C(9)-C(10)-H(10)	119.6	C(1)-N(2)-H(2)	116.5
C(5)-C(10)-H(10)	119.6	C(8)-O(4)-H(4)	109.5
C(12)-C(11)-C(16)	118.60(17)	C(14)-O(5)-H(5)	109.5
C(12)-C(11)-C(3)	121.06(17)		

Table A1-4. Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	22(1)	22(1)	14(1)	0(1)	-2(1)	2(1)
C(2)	24(1)	22(1)	17(1)	0(1)	0(1)	2(1)
C(3)	24(1)	21(1)	13(1)	1(1)	-1(1)	-1(1)
C(4)	19(1)	25(1)	15(1)	1(1)	-2(1)	1(1)
C(5)	20(1)	22(1)	18(1)	0(1)	1(1)	-2(1)
C(6)	23(1)	23(1)	16(1)	0(1)	-3(1)	-3(1)
C(7)	22(1)	24(1)	23(1)	3(1)	-5(1)	0(1)
C(8)	21(1)	20(1)	20(1)	1(1)	4(1)	-3(1)
C(9)	27(1)	27(1)	16(1)	-2(1)	-1(1)	-1(1)
C(10)	25(1)	28(1)	15(1)	2(1)	-2(1)	2(1)
C(11)	23(1)	28(1)	12(1)	0(1)	-1(1)	1(1)
C(12)	28(1)	24(1)	22(1)	1(1)	-1(1)	3(1)
C(13)	25(1)	31(1)	28(1)	-1(1)	-2(1)	-3(1)
C(14)	24(1)	38(1)	21(1)	-1(1)	-1(1)	6(1)
C(15)	33(1)	28(1)	29(1)	-1(1)	-4(1)	8(1)
C(16)	30(1)	26(1)	25(1)	-2(1)	-3(1)	1(1)
N(1)	25(1)	21(1)	14(1)	1(1)	1(1)	-4(1)

Table A1-4 (continuation)

N(2)	26(1)	28(1)	11(1)	-1(1)	2(1)	-2(1)
O(1)	31(1)	24(1)	19(1)	-2(1)	-2(1)	-4(1)
O(2)	41(1)	33(1)	12(1)	1(1)	0(1)	-10(1)
O(3)	29(1)	32(1)	17(1)	4(1)	0(1)	-8(1)
O(4)	27(1)	22(1)	23(1)	-2(1)	-1(1)	1(1)
O(5)	24(1)	41(1)	40(1)	2(1)	-4(1)	7(1)

Table A1-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2 \times 10^3$).

	x	y	z	U(eq)
H(6)	4475	697	9333	25
H(7)	4901	-1549	8187	28
H(9)	4098	-1326	3020	28
H(10)	3685	943	4150	27
H(12)	3019	516	6905	30
H(13)	2162	889	6026	33
H(15)	2392	5601	5906	36
H(16)	3252	5209	6714	32
H(1)	4556	5632	7352	24
H(2)	3932	3946	12076	26
H(4)	4672	-3299	3831	36
H(5)	1613	4387	5276	52

Table A1-6. Hydrogen bonds for 2008JT1 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(4)#1	0.88	2.11	2.915(2)	152.0
N(2)-H(2)...O(2)#2	0.88	1.97	2.772(2)	151.0
O(4)-H(4)...O(1)#3	0.84	2.06	2.889(2)	167.9
O(5)-H(5)...O(3)#4	0.84	1.98	2.805(2)	168.5

Symmetry transformations used to generate equivalent atoms:
#1 x,y+1,z #2 x,y,z+1 #3 x,y-1,z-1 #4 -x+1/2,y+1/2,z-1/2

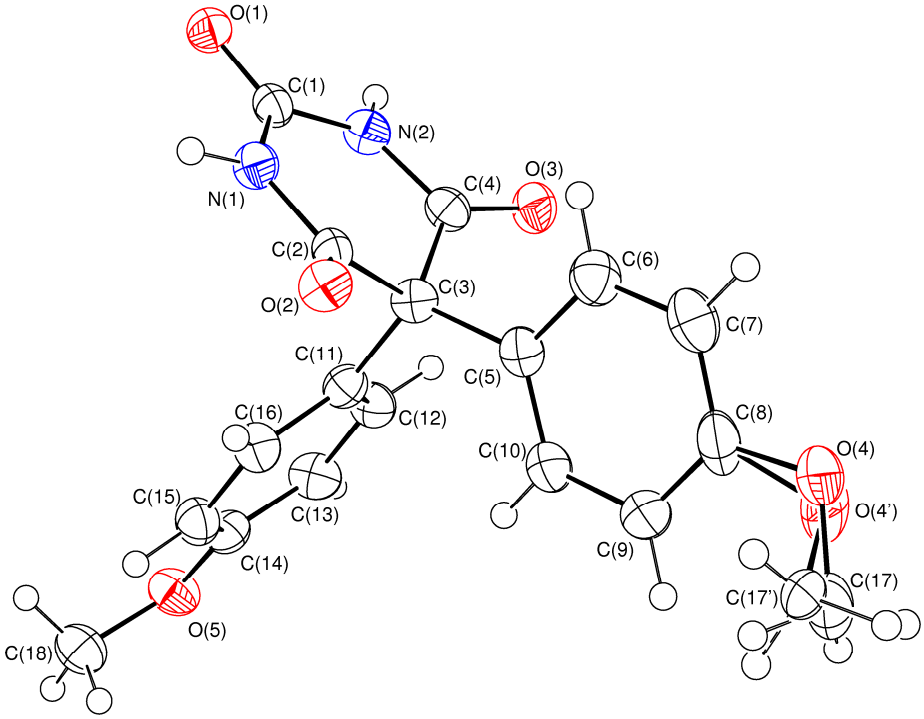


Figure A1-12. X-ray structure of **39**, centered on a single molecule.

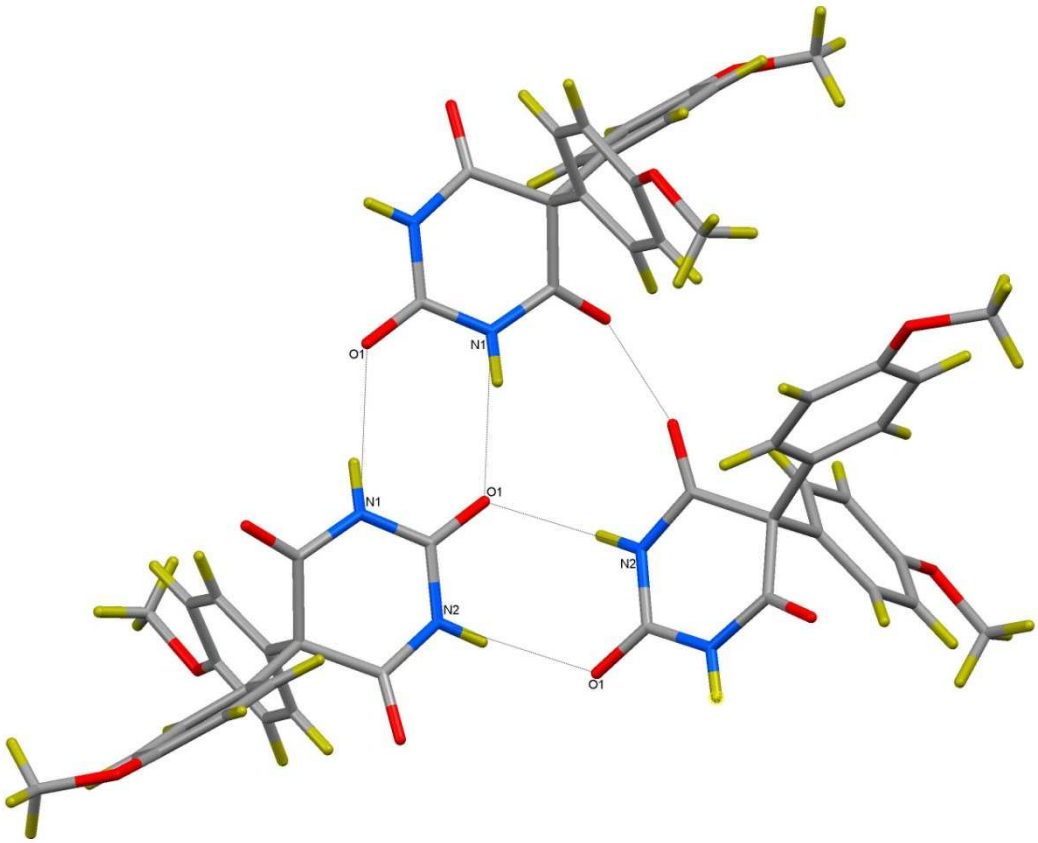


Figure A1-13. X-ray structure of **39** showing intermolecular interactions.

Table A1-7. Crystal data and structure refinement.

Empirical formula	$C_{18}\ H_{16}\ N_2\ O_5$	
Formula weight	340.33	
Temperature	120(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 15.5044(3) Å	α= 90°.
	b = 16.0007(3) Å	β= 112.0540(10)°.
	c = 13.7051(2) Å	γ = 90°.
Volume	3151.20(10) $Å^3$	
Z	8	
Density (calculated)	1.435 Mg/m^3	
Absorption coefficient	0.887 mm^{-1}	
F(000)	1424	
Crystal size	0.36 x 0.30 x 0.10 mm^3	
Theta range for data collection	6.54 to 66.58°.	
Index ranges	-18<=h<=18, -18<=k<=19, -16<=l<=15	
Reflections collected	11708	
Independent reflections	2644 [R(int) = 0.0260]	
Completeness to theta = 66.58°	94.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9165 and 0.7407	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2644 / 18 / 248	
Goodness-of-fit on F^2	1.193	
Final R indices [I>2sigma(I)]	R1 = 0.0525, wR2 = 0.1584	
R indices (all data)	R1 = 0.0684, wR2 = 0.2331	
Largest diff. peak and hole	0.336 and -0.372 e.$Å^{-3}$	

Notes:

The group O(4)-C(17) is disordered over two sites with O(4)-C(17) being present at 72 % occupancy and O(4')-C(17') being present at 28 % occupancy.
The hydrogen atoms were fixed as riding models.
The hydrogen bonding is detailed in Table 6.

Table A1-8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	783(2)	139(2)	6602(2)	26(1)
C(2)	2179(2)	-515(2)	6501(2)	26(1)
C(3)	2763(2)	-175(2)	7597(2)	28(1)
C(4)	2149(2)	-43(2)	8236(2)	30(1)

Table A1-8 (continuation)

	x	y	z	U(eq)
C(5)	3549(2)	-789(2)	8154(2)	30(1)
C(6)	3305(2)	-1600(2)	8328(2)	39(1)
C(7)	3962(2)	-2213(2)	8718(2)	41(1)
C(8)	4895(2)	-2023(2)	8969(2)	42(1)
C(9)	5151(2)	-1228(2)	8826(3)	47(1)
C(10)	4474(2)	-608(2)	8427(2)	40(1)
C(11)	3110(2)	703(2)	7431(2)	28(1)
C(12)	3301(2)	1311(2)	8210(2)	32(1)
C(13)	3610(2)	2095(2)	8065(2)	37(1)
C(14)	3726(2)	2283(2)	7131(2)	30(1)
C(15)	3570(2)	1673(2)	6369(2)	33(1)
C(16)	3263(2)	889(2)	6527(2)	32(1)
O(4)	5450(4)	-2731(4)	9266(7)	38(1)
C(17)	6342(6)	-2654(10)	9202(9)	45(2)
O(4')	5681(14)	-2496(15)	9515(13)	48(3)
C(17')	6165(18)	-2740(20)	8850(20)	43(5)
C(18)	4066(2)	3298(2)	6060(2)	41(1)
N(1)	1270(2)	-212(1)	6059(2)	29(1)
N(2)	1251(2)	217(1)	7670(2)	30(1)
O(1)	-34(1)	341(1)	6176(1)	30(1)
O(2)	2474(1)	-973(1)	6010(1)	32(1)
O(3)	2424(1)	-110(1)	9183(1)	36(1)
O(5)	3969(2)	3087(1)	7027(2)	38(1)

Table A1-9. Bond lengths [Å] and angles [°].

C(1)-O(1)	1.223(3)	C(9)-C(10)	1.397(4)
C(1)-N(1)	1.364(3)	C(9)-H(9)	0.9500
C(1)-N(2)	1.374(3)	C(10)-H(10)	0.9500
C(2)-O(2)	1.196(3)	C(11)-C(16)	1.379(4)
C(2)-N(1)	1.395(3)	C(11)-C(12)	1.390(4)
C(2)-C(3)	1.534(4)	C(12)-C(13)	1.384(4)
C(3)-C(5)	1.528(4)	C(12)-H(12)	0.9500
C(3)-C(4)	1.532(4)	C(13)-C(14)	1.391(4)
C(3)-C(11)	1.551(4)	C(13)-H(13)	0.9500
C(4)-O(3)	1.208(3)	C(14)-O(5)	1.364(3)
C(4)-N(2)	1.379(4)	C(14)-C(15)	1.381(4)
C(5)-C(10)	1.371(4)	C(15)-C(16)	1.388(4)
C(5)-C(6)	1.396(4)	C(15)-H(15)	0.9500
C(6)-C(7)	1.371(4)	C(16)-H(16)	0.9500
C(6)-H(6)	0.9500	O(4)-C(17)	1.423(7)
C(7)-C(8)	1.389(5)	C(17)-H(17A)	0.9800
C(7)-H(7)	0.9500	C(17)-H(17B)	0.9800
C(8)-C(9)	1.368(4)	C(17)-H(17C)	0.9800
C(8)-O(4)	1.388(5)	O(4')-C(17')	1.429(10)
C(8)-O(4')	1.390(9)	C(17')-H(17D)	0.9800

Table A1-9 (continuation)

C(17')-H(17E)	0.9800	C(18)-H(18B)	0.9800
C(17')-H(17F)	0.9800	C(18)-H(18C)	0.9800
C(18)-O(5)	1.429(4)	N(1)-H(1)	0.8800
C(18)-H(18A)	0.9800	N(2)-H(2)	0.8800

O(1)-C(1)-N(1)	122.4(2)	C(12)-C(11)-C(3)	120.4(2)
O(1)-C(1)-N(2)	121.5(2)	C(13)-C(12)-C(11)	120.6(3)
N(1)-C(1)-N(2)	116.1(2)	C(13)-C(12)-H(12)	119.7
O(2)-C(2)-N(1)	120.4(2)	C(11)-C(12)-H(12)	119.7
O(2)-C(2)-C(3)	124.0(2)	C(12)-C(13)-C(14)	119.9(3)
N(1)-C(2)-C(3)	115.5(2)	C(12)-C(13)-H(13)	120.0
C(5)-C(3)-C(4)	110.7(2)	C(14)-C(13)-H(13)	120.0
C(5)-C(3)-C(2)	109.1(2)	O(5)-C(14)-C(15)	124.3(3)
C(4)-C(3)-C(2)	110.1(2)	O(5)-C(14)-C(13)	115.9(2)
C(5)-C(3)-C(11)	113.6(2)	C(15)-C(14)-C(13)	119.8(3)
C(4)-C(3)-C(11)	106.5(2)	C(14)-C(15)-C(16)	119.6(3)
C(2)-C(3)-C(11)	106.7(2)	C(14)-C(15)-H(15)	120.2
O(3)-C(4)-N(2)	120.4(2)	C(16)-C(15)-H(15)	120.2
O(3)-C(4)-C(3)	123.8(3)	C(11)-C(16)-C(15)	121.3(3)
N(2)-C(4)-C(3)	115.7(2)	C(11)-C(16)-H(16)	119.4
C(10)-C(5)-C(6)	118.2(3)	C(15)-C(16)-H(16)	119.4
C(10)-C(5)-C(3)	123.8(2)	C(8)-O(4)-C(17)	114.9(7)
C(6)-C(5)-C(3)	117.9(2)	C(8)-O(4')-C(17')	111.5(17)
C(7)-C(6)-C(5)	121.5(3)	O(4')-C(17')-H(17D)	109.5
C(7)-C(6)-H(6)	119.3	O(4')-C(17')-H(17E)	109.5
C(5)-C(6)-H(6)	119.3	H(17D)-C(17')-H(17E)	109.5
C(6)-C(7)-C(8)	119.5(3)	O(4')-C(17')-H(17F)	109.5
C(6)-C(7)-H(7)	120.2	H(17D)-C(17')-H(17F)	109.5
C(8)-C(7)-H(7)	120.2	H(17E)-C(17')-H(17F)	109.5
C(9)-C(8)-O(4)	128.3(4)	O(5)-C(18)-H(18A)	109.5
C(9)-C(8)-C(7)	119.9(3)	O(5)-C(18)-H(18B)	109.5
O(4)-C(8)-C(7)	111.6(4)	H(18A)-C(18)-H(18B)	109.5
C(9)-C(8)-O(4')	109.9(12)	O(5)-C(18)-H(18C)	109.5
O(4)-C(8)-O(4')	22.5(9)	H(18A)-C(18)-H(18C)	109.5
C(7)-C(8)-O(4')	129.4(12)	H(18B)-C(18)-H(18C)	109.5
C(8)-C(9)-C(10)	120.0(3)	C(1)-N(1)-C(2)	125.6(2)
C(8)-C(9)-H(9)	120.0	C(1)-N(1)-H(1)	117.2
C(10)-C(9)-H(9)	120.0	C(2)-N(1)-H(1)	117.2
C(5)-C(10)-C(9)	120.8(3)	C(1)-N(2)-C(4)	126.1(2)
C(5)-C(10)-H(10)	119.6	C(1)-N(2)-H(2)	116.9
C(9)-C(10)-H(10)	119.6	C(4)-N(2)-H(2)	116.9
C(16)-C(11)-C(12)	118.7(3)	C(14)-O(5)-C(18)	116.8(2)
C(16)-C(11)-C(3)	120.8(2)		

Table A1-10. Anisotropic displacement parameters ($Å^2 \times 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	31(1)	26(1)	22(1)	0(1)	10(1)	-4(1)
C(2)	30(1)	26(1)	22(1)	1(1)	9(1)	-2(1)
C(3)	30(1)	28(1)	28(1)	-4(1)	12(1)	-1(1)
C(4)	34(1)	27(1)	31(2)	-1(1)	14(1)	-2(1)
C(5)	36(1)	29(1)	28(1)	1(1)	15(1)	5(1)
C(6)	43(2)	32(2)	38(2)	1(1)	12(1)	-1(1)
C(7)	59(2)	29(1)	38(2)	2(1)	21(1)	1(1)
C(8)	54(2)	39(2)	37(2)	15(1)	22(1)	16(1)
C(9)	33(2)	54(2)	58(2)	22(2)	21(2)	9(1)
C(10)	37(2)	38(2)	45(2)	15(1)	17(1)	4(1)
C(11)	26(1)	30(1)	30(1)	-2(1)	10(1)	3(1)
C(12)	35(1)	34(2)	29(1)	-4(1)	14(1)	-1(1)
C(13)	40(2)	36(2)	37(2)	-10(1)	17(1)	-7(1)
C(14)	28(1)	28(1)	32(1)	-4(1)	7(1)	-3(1)
C(15)	36(1)	34(2)	29(1)	1(1)	12(1)	-1(1)
C(16)	37(2)	29(1)	30(1)	-3(1)	13(1)	-1(1)
O(4)	43(2)	28(2)	43(3)	10(2)	15(2)	5(2)
C(17)	51(5)	45(4)	43(6)	17(4)	22(4)	18(4)
O(4')	61(7)	38(7)	49(7)	14(5)	24(5)	27(6)
C(17')	28(8)	48(11)	55(14)	27(11)	20(9)	18(7)
C(18)	47(2)	31(2)	46(2)	1(1)	20(1)	-6(1)
N(1)	30(1)	34(1)	22(1)	-4(1)	11(1)	-1(1)
N(2)	33(1)	30(1)	29(1)	-4(1)	15(1)	0(1)
O(1)	28(1)	31(1)	31(1)	1(1)	11(1)	2(1)
O(2)	34(1)	33(1)	31(1)	-6(1)	13(1)	1(1)
O(3)	40(1)	46(1)	22(1)	0(1)	11(1)	0(1)
O(5)	45(1)	31(1)	41(1)	-6(1)	19(1)	-9(1)

Table A1-11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	U(eq)
H(6)	2669	-1729	8174	46
H(7)	3781	-2764	8815	49
H(9)	5789	-1097	8999	57
H(10)	4658	-55	8344	48
H(12)	3217	1187	8846	39
H(13)	3744	2505	8603	44
H(15)	3671	1791	5741	40
H(16)	3157	471	6001	38
H(17A)	6268	-2504	8481	68
H(17B)	6674	-3187	9393	68
H(17C)	6699	-2217	9688	68
H(17D)	5718	-2943	8181	64

H(17E)	6614	-3177	9200	64
H(17F)	6494	-2251	8727	64
H(18A)	4540	2940	5962	61
H(18B)	4255	3885	6082	61
H(18C)	3470	3216	5473	61
H(1)	987	-251	5372	34
H(2)	950	456	8026	36

Table A1-12. Hydrogen bonds for 2008JT3 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)#1	0.88	2.09	2.948(3)	166.6
N(2)-H(2)...O(1)#2	0.88	2.10	2.887(3)	148.7

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y,-z+1 #2 -x,y,-z+3/2

42

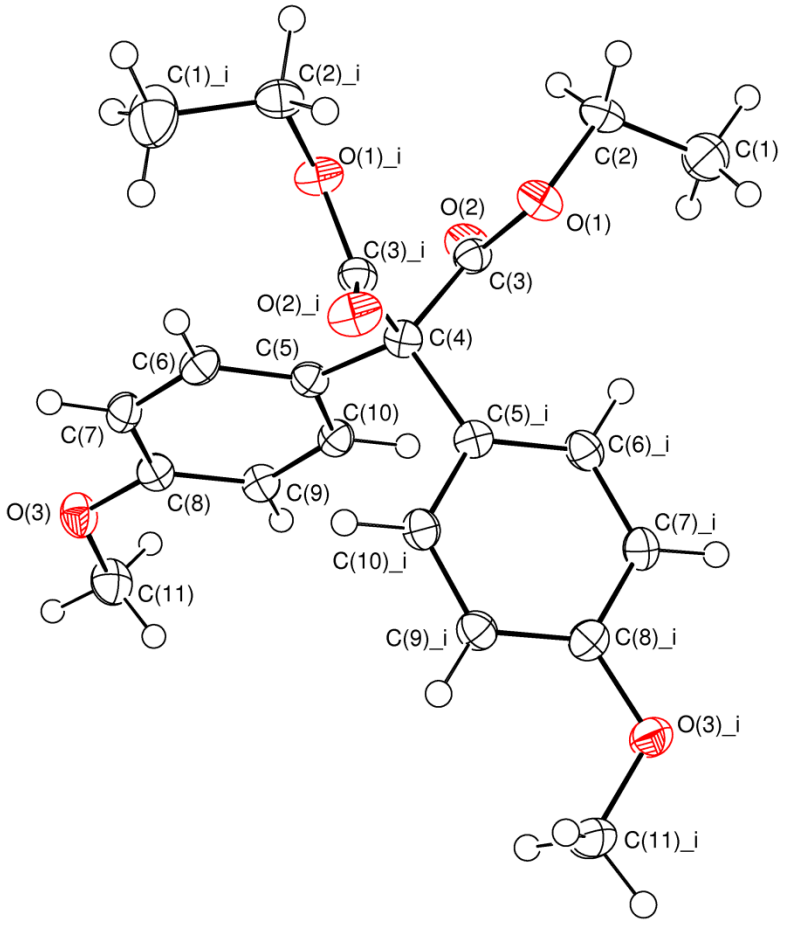


Figure A1-14. X-ray structure of **42**, centered on a single molecule.

Table A1-13. Crystal data and structure refinement.

Identification code	2008JT4, AS03	
Empirical formula	C_{21} H_{24} O_6	
Formula weight	372.40	
Temperature	120(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	A b a 2	
Unit cell dimensions	a = 13.2464(4) Å	α= 90°.
	b = 19.3987(7) Å	β= 90°.
	c = 7.3360(3) Å	γ = 90°.
Volume	1885.08(12) $Å^3$	
Z	4	
Density (calculated)	1.312 Mg/m^3	
Absorption coefficient	0.791 mm^{-1}	
F(000)	792	
Crystal size	0.24 x 0.10 x 0.02 mm^3	
Theta range for data collection	6.68 to 69.90°.	
Index ranges	-15<=h<=15, -23<=k<=23, -7<=l<=8	
Reflections collected	8733	
Independent reflections	1594 [R(int) = 0.0277]	
Completeness to theta = 69.90°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9844 and 0.8329	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1594 / 1 / 125	
Goodness-of-fit on F^2	1.095	
Final R indices [I>2sigma(I)]	R1 = 0.0270, wR2 = 0.0688	
R indices (all data)	R1 = 0.0285, wR2 = 0.0701	
Absolute structure parameter	0.01(18)	
Largest diff. peak and hole	0.137 and -0.146 e.$Å^{-3}$	

Notes:
Atom C(4) lies on a two-fold rotation axis such that only half of the molecule is crystallographically unique.
The hydrogen atoms were fixed as riding models.

Table A1-14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-1714(2)	-1525(1)	-2655(3)	49(1)
C(2)	-1216(1)	-860(1)	-3170(2)	26(1)
C(3)	-862(1)	-246(1)	-458(2)	21(1)
C(4)	0	0	803(3)	21(1)
C(5)	-362(1)	593(1)	2032(2)	21(1)

Table A1-14 (continuation)

	x	y	z	U(eq)
C(6)	52(1)	1254(1)	2009(2)	24(1)
C(7)	-244(1)	1744(1)	3279(2)	24(1)
C(8)	-954(1)	1586(1)	4600(2)	23(1)
C(9)	-1399(1)	935(1)	4609(2)	23(1)
C(10)	-1098(1)	451(1)	3331(2)	22(1)
C(11)	-1816(1)	1904(1)	7317(2)	33(1)
O(1)	-497(1)	-641(1)	-1788(1)	25(1)
O(2)	-1738(1)	-111(1)	-247(2)	29(1)
O(3)	-1173(1)	2094(1)	5833(2)	29(1)

Table A1-15. Bond lengths [Å] and angles [°].

C(1)-C(2)	1.496(2)	C(5)-C(6)	1.3953(18)
C(1)-H(1A)	0.9800	C(6)-C(7)	1.388(2)
C(1)-H(1B)	0.9800	C(6)-H(6)	0.9500
C(1)-H(1C)	0.9800	C(7)-C(8)	1.384(2)
C(2)-O(1)	1.4545(17)	C(7)-H(7)	0.9500
C(2)-H(2A)	0.9900	C(8)-O(3)	1.3677(18)
C(2)-H(2B)	0.9900	C(8)-C(9)	1.3948(18)
C(3)-O(2)	1.2007(16)	C(9)-C(10)	1.385(2)
C(3)-O(1)	1.3305(18)	C(9)-H(9)	0.9500
C(3)-C(4)	1.5449(19)	C(10)-H(10)	0.9500
C(4)-C(5)	1.5385(18)	C(11)-O(3)	1.4297(19)
C(4)-C(5)#1	1.5385(18)	C(11)-H(11A)	0.9800
C(4)-C(3)#1	1.5448(19)	C(11)-H(11B)	0.9800
C(5)-C(10)	1.391(2)	C(11)-H(11C)	0.9800

C(2)-C(1)-H(1A)	109.5	C(5)#1-C(4)-C(3)	110.49(7)
C(2)-C(1)-H(1B)	109.5	C(3)#1-C(4)-C(3)	106.45(17)
H(1A)-C(1)-H(1B)	109.5	C(10)-C(5)-C(6)	117.81(13)
C(2)-C(1)-H(1C)	109.5	C(10)-C(5)-C(4)	118.16(11)
H(1A)-C(1)-H(1C)	109.5	C(6)-C(5)-C(4)	123.88(12)
H(1B)-C(1)-H(1C)	109.5	C(7)-C(6)-C(5)	120.68(13)
O(1)-C(2)-C(1)	111.40(13)	C(7)-C(6)-H(6)	119.7
O(1)-C(2)-H(2A)	109.3	C(5)-C(6)-H(6)	119.7
C(1)-C(2)-H(2A)	109.3	C(8)-C(7)-C(6)	120.69(12)
O(1)-C(2)-H(2B)	109.3	C(8)-C(7)-H(7)	119.7
C(1)-C(2)-H(2B)	109.3	C(6)-C(7)-H(7)	119.7
H(2A)-C(2)-H(2B)	108.0	O(3)-C(8)-C(7)	116.60(11)
O(2)-C(3)-O(1)	124.83(14)	O(3)-C(8)-C(9)	124.02(13)
O(2)-C(3)-C(4)	124.73(13)	C(7)-C(8)-C(9)	119.38(13)
O(1)-C(3)-C(4)	110.43(10)	C(10)-C(9)-C(8)	119.32(13)
C(5)-C(4)-C(5)#1	108.23(17)	C(10)-C(9)-H(9)	120.3
C(5)-C(4)-C(3)#1	110.49(7)	C(8)-C(9)-H(9)	120.3
C(5)#1-C(4)-C(3)#1	110.60(7)	C(9)-C(10)-C(5)	122.05(12)
C(5)-C(4)-C(3)	110.60(7)	C(9)-C(10)-H(10)	119.0

Table A1-15 (continuation)

		O(3)-C(11)-H(11C)	109.5
C(5)-C(10)-H(10)	119.0	H(11A)-C(11)-H(11C)	109.5
O(3)-C(11)-H(11A)	109.5	H(11B)-C(11)-H(11C)	109.5
O(3)-C(11)-H(11B)	109.5	C(3)-O(1)-C(2)	116.28(10)
H(11A)-C(11)-H(11B)	109.5	C(8)-O(3)-C(11)	116.38(10)

Table A1-16. Anisotropic displacement parameters ($Å^2 x\ 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	63(1)	39(1)	45(1)	4(1)	-24(1)	-15(1)
C(2)	26(1)	33(1)	20(1)	-2(1)	-4(1)	2(1)
C(3)	22(1)	22(1)	20(1)	1(1)	0(1)	2(1)
C(4)	18(1)	23(1)	22(1)	0	0	0(1)
C(5)	18(1)	23(1)	21(1)	0(1)	-2(1)	2(1)
C(6)	21(1)	25(1)	25(1)	4(1)	3(1)	-1(1)
C(7)	23(1)	21(1)	28(1)	2(1)	0(1)	-3(1)
C(8)	20(1)	23(1)	26(1)	-1(1)	-1(1)	2(1)
C(9)	20(1)	25(1)	24(1)	1(1)	2(1)	-1(1)
C(10)	19(1)	22(1)	25(1)	2(1)	-1(1)	-2(1)
C(11)	35(1)	32(1)	32(1)	-7(1)	9(1)	1(1)
O(1)	20(1)	33(1)	23(1)	-5(1)	-1(1)	3(1)
O(2)	18(1)	39(1)	30(1)	-6(1)	-1(1)	4(1)
O(3)	30(1)	26(1)	30(1)	-6(1)	7(1)	-3(1)

Table A1-17. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$)

	x	y	z	U(eq)
H(1A)	-2139	-1452	-1579	74
H(1B)	-1197	-1870	-2378	74
H(1C)	-2132	-1687	-3670	74
H(2A)	-861	-919	-4348	32
H(2B)	-1737	-500	-3330	32
H(6)	543	1370	1115	28
H(7)	43	2193	3242	29
H(9)	-1902	824	5484	28
H(10)	-1405	8	3341	26
H(11A)	-1528	1505	7950	49
H(11B)	-2486	1785	6848	49
H(11C)	-1872	2291	8168	49

18•39

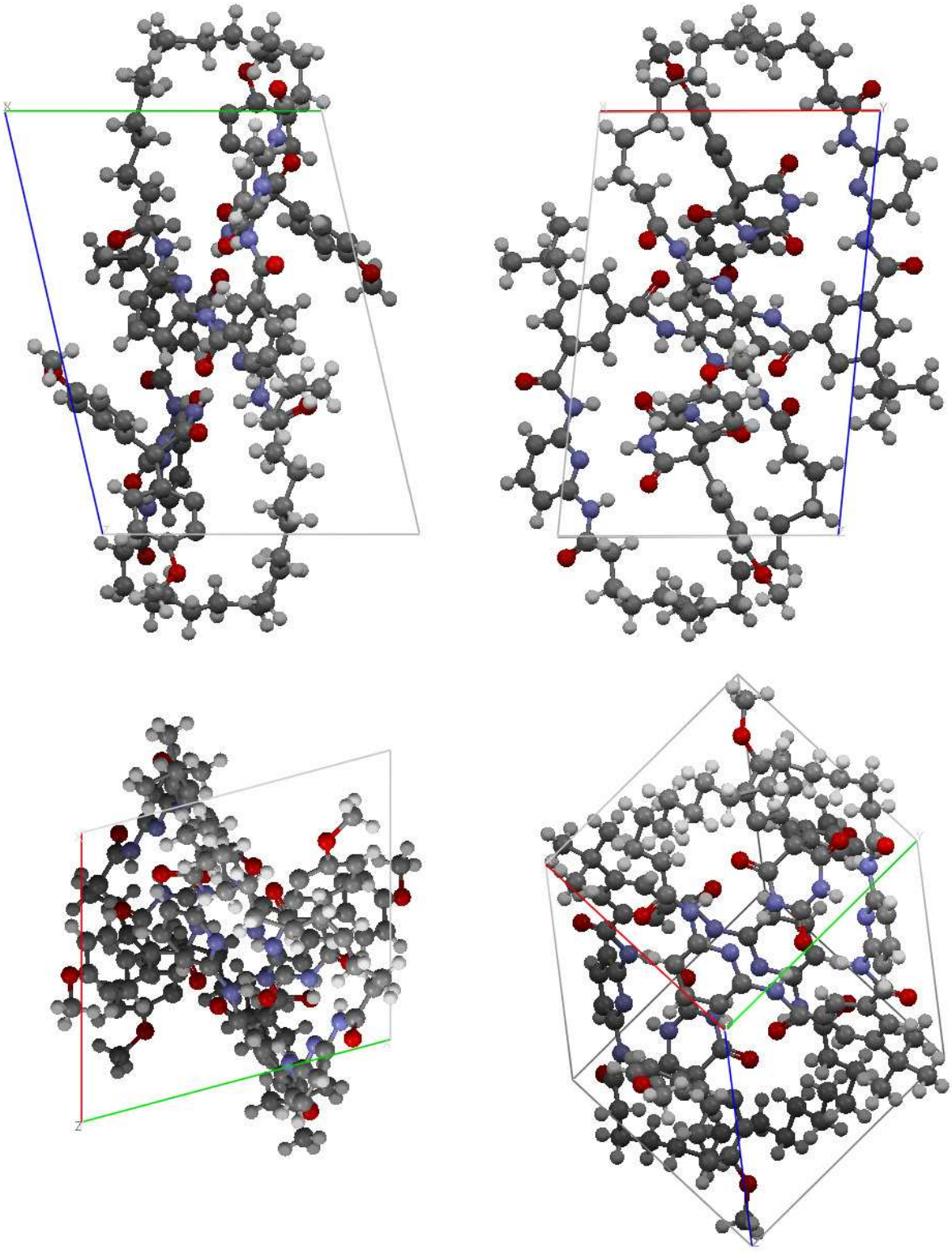


Figure A1-15. X-ray structure of **18•39** complex along three axes and in perspective.

The crystals belong to the triclinic P-1 space group with unit cell parameters a = 12.122 Å, b = 13.6901 Å, c = 18.2778 Å, α = 74.873°, β = 80.319°, γ = 73.177°. Mr = 995.17, V = 2788.69 $Å^3$, ρ_{calc} = 1.185 $g.cm^{-3}$

The planar angles have been calculated using Mercury on the **18•39** complex. In a first time, the nitrogen atoms of the receptor and the ring of the barbiturate have been used to define the two planes. An angle of 29.8° has been measured (shown in **Figure A1-14**). However, it was observed that the two pyridine moieties were not actually co-planar. The planes of the two pyridine moieties intersect with the plane of the barbiturate along the direction of the N-H···N H-bonds, with angles of 31.1° and 36.4°, and the two pyridine planes intersect with an angle of 59.6° (see **Figure A1.15**).

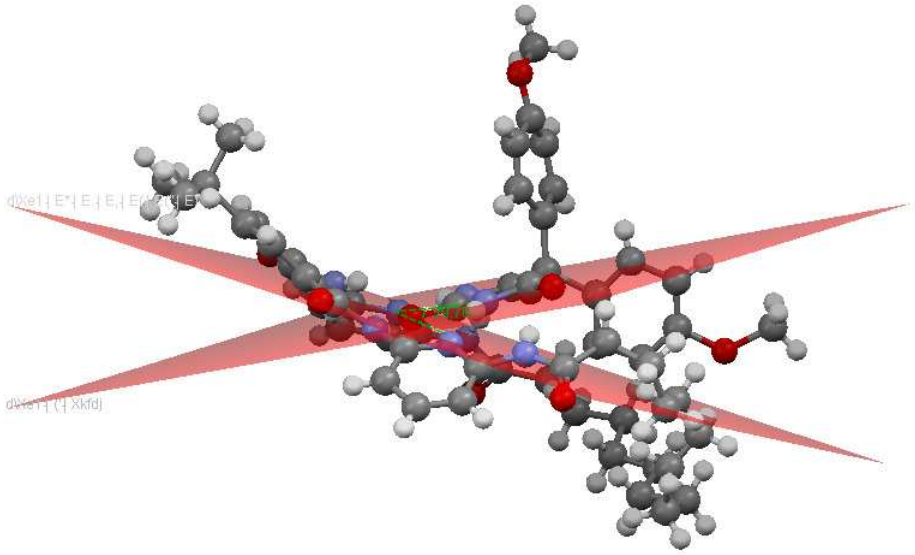


Figure A1-16. X-ray structure of the **18•39** complex showing molecular planes with intermolecular angle of 29.8°.

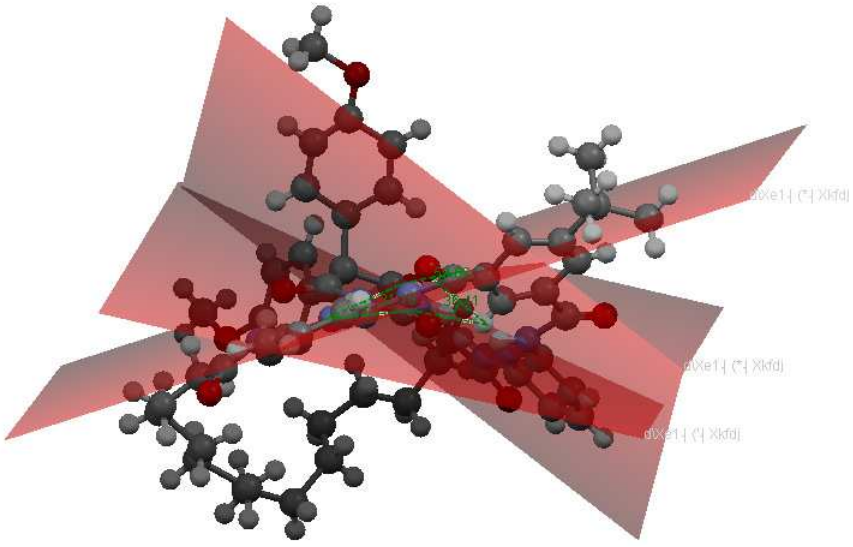


Figure A1-17. X-ray structure of the **18•39** complex showing the angles between the plane of the barbiturate and the planes of the two pyridine moieties of the receptor (31.1° and 36.4°), and the angle between the two pyridine planes (59.6°).

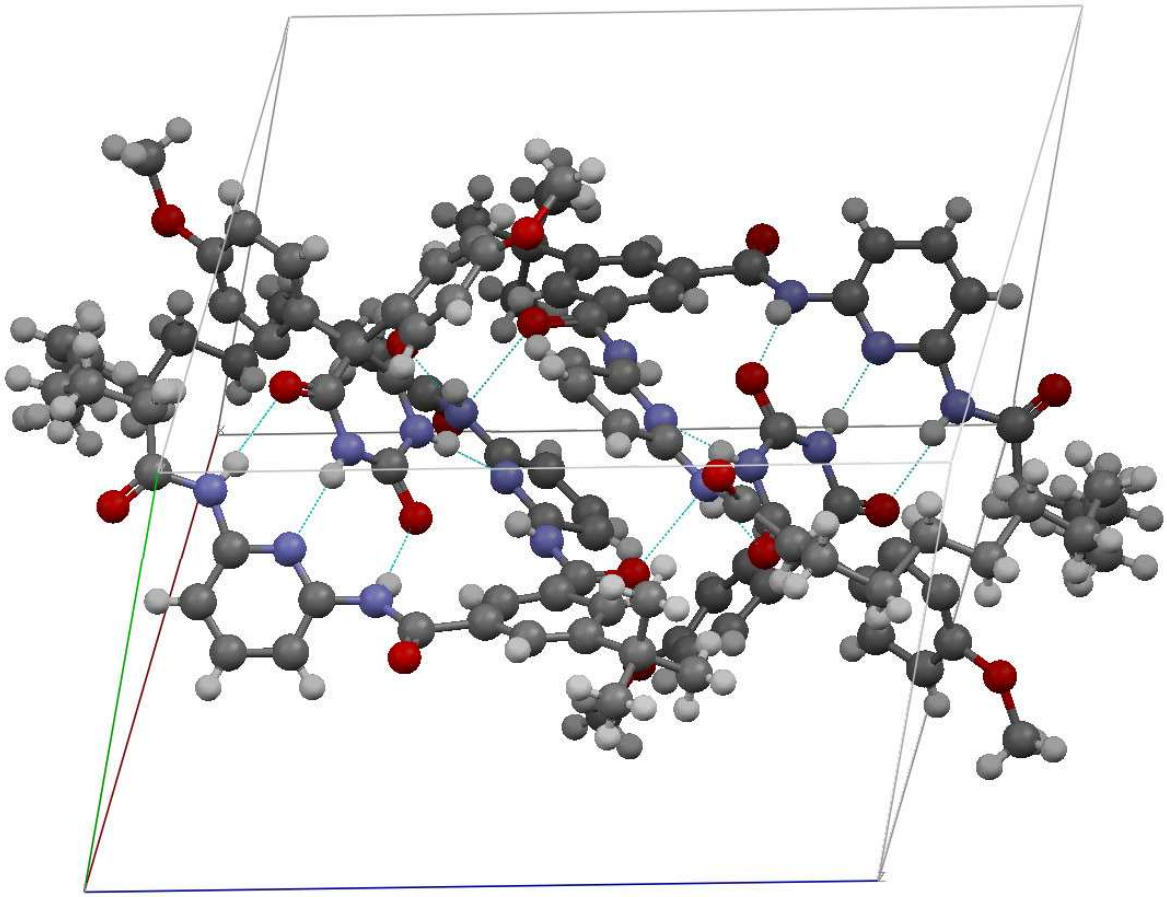


Figure A1.18. Partial X-ray structure of the **18•39** complex showing hydrogen bonds.

APPENDIX 2

Mass spectra

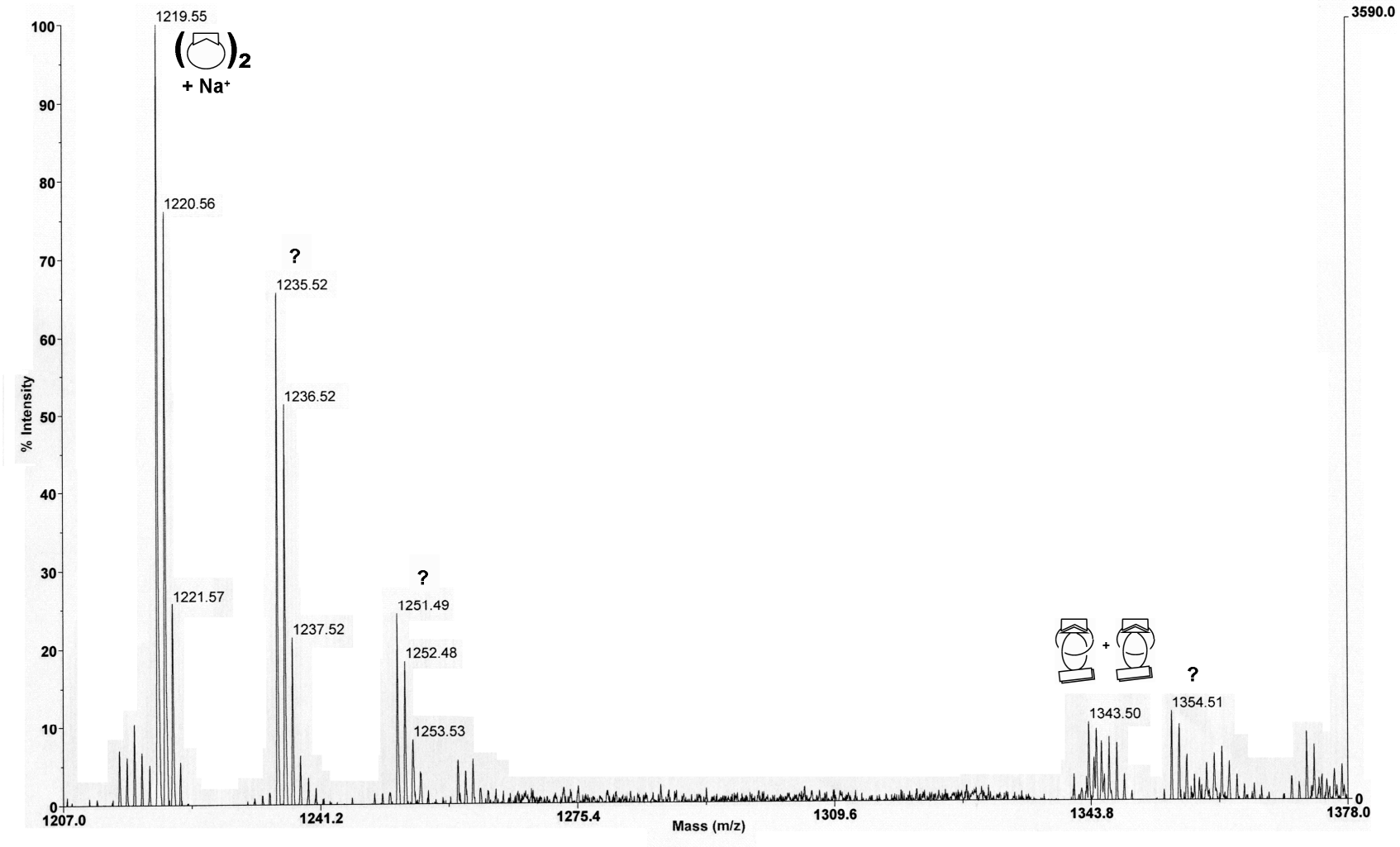
MALDI spectra of experiments with anthracene-tagged barbiturate 34

These spectra were performed by the CESAMO (Bordeaux, France) on a Voyager mass spectrometer (Applied Biosystems). The instrument is equipped with a pulsed N2 laser (337 nm) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron and with an accelerating voltage of 20 kV. Samples were dissolved in CHCl3 at 10 mg/ml. The dithranol matrix solution was prepared by dissolving 10 mg in 1 ml of CHCl3. A MeOH solution of cationisation agent (NaI, 10 mg/ml) was also prepared. The solutions were combined in a 10:1:1 volume ratio of matrix to sample to cationisation agent. One to two microliters of the obtained solution was deposited onto the sample target and vacuum-dried.

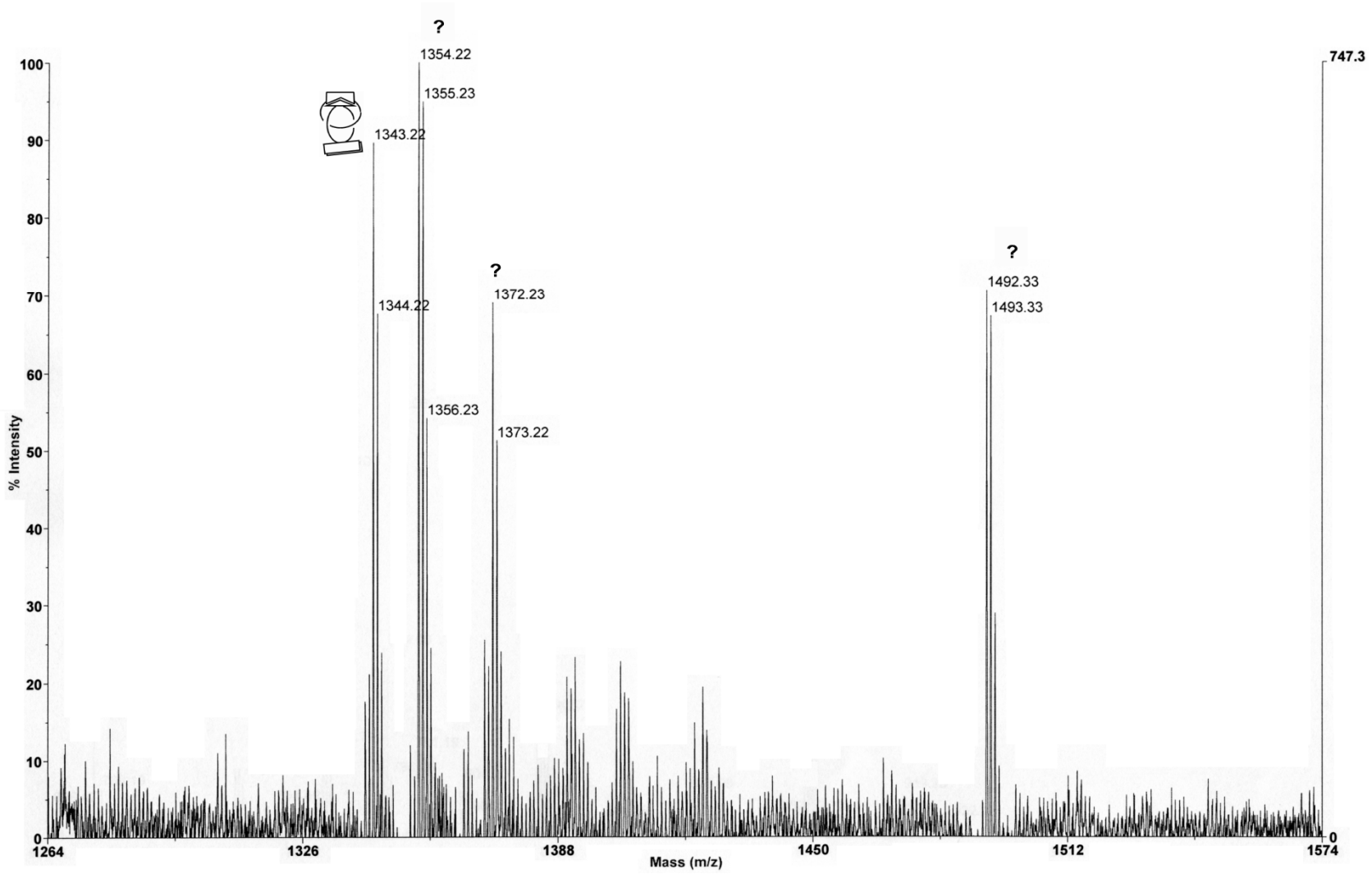
MALDI and ES^+ spectra with trityl terminated 36 and olefin-terminated receptors, and ES^- spectra of experiments with olefin-terminated barbiturate 37 and reduced receptors

These spectra were performed in Birmingham on a Bruker Biflex IV Maldi Time of Flight Mass Spectrometer.

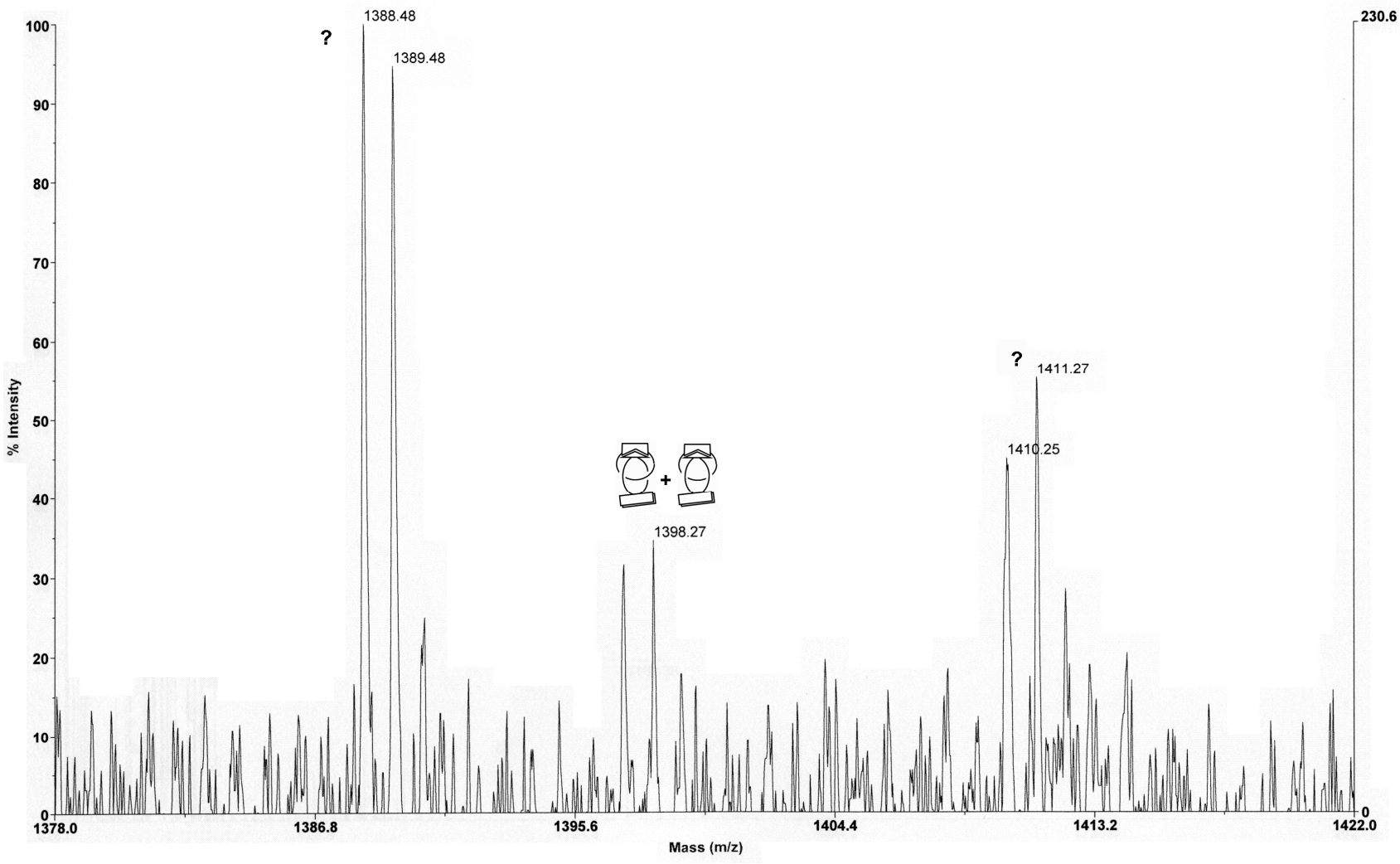
MALDI of 1:1 mixture of **34** and **17**, after irradiation, detail:



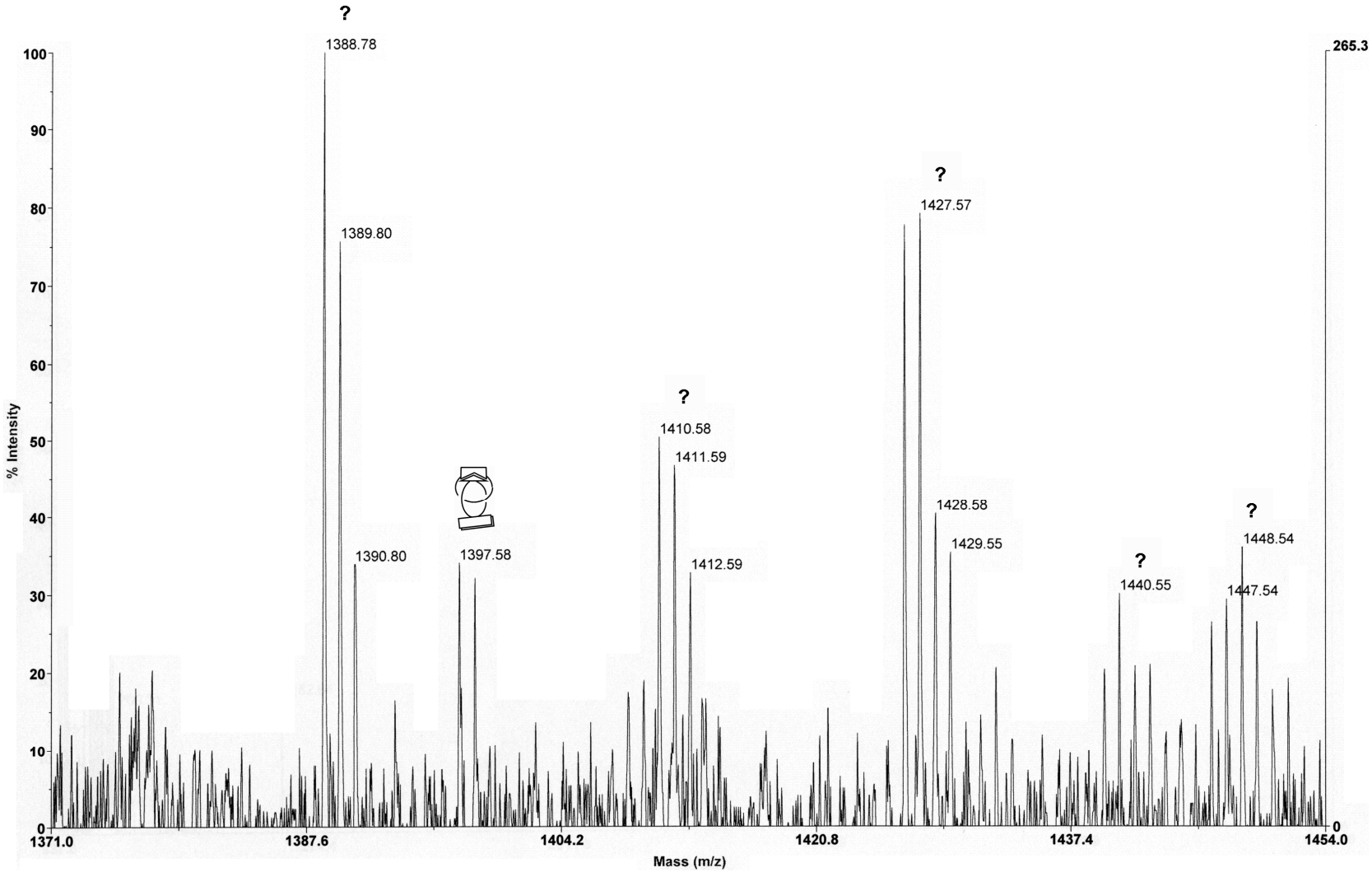
MALDI of 1:1 mixture of **34** and **17**, after irradiation and addition of an excess of barbital, detail:



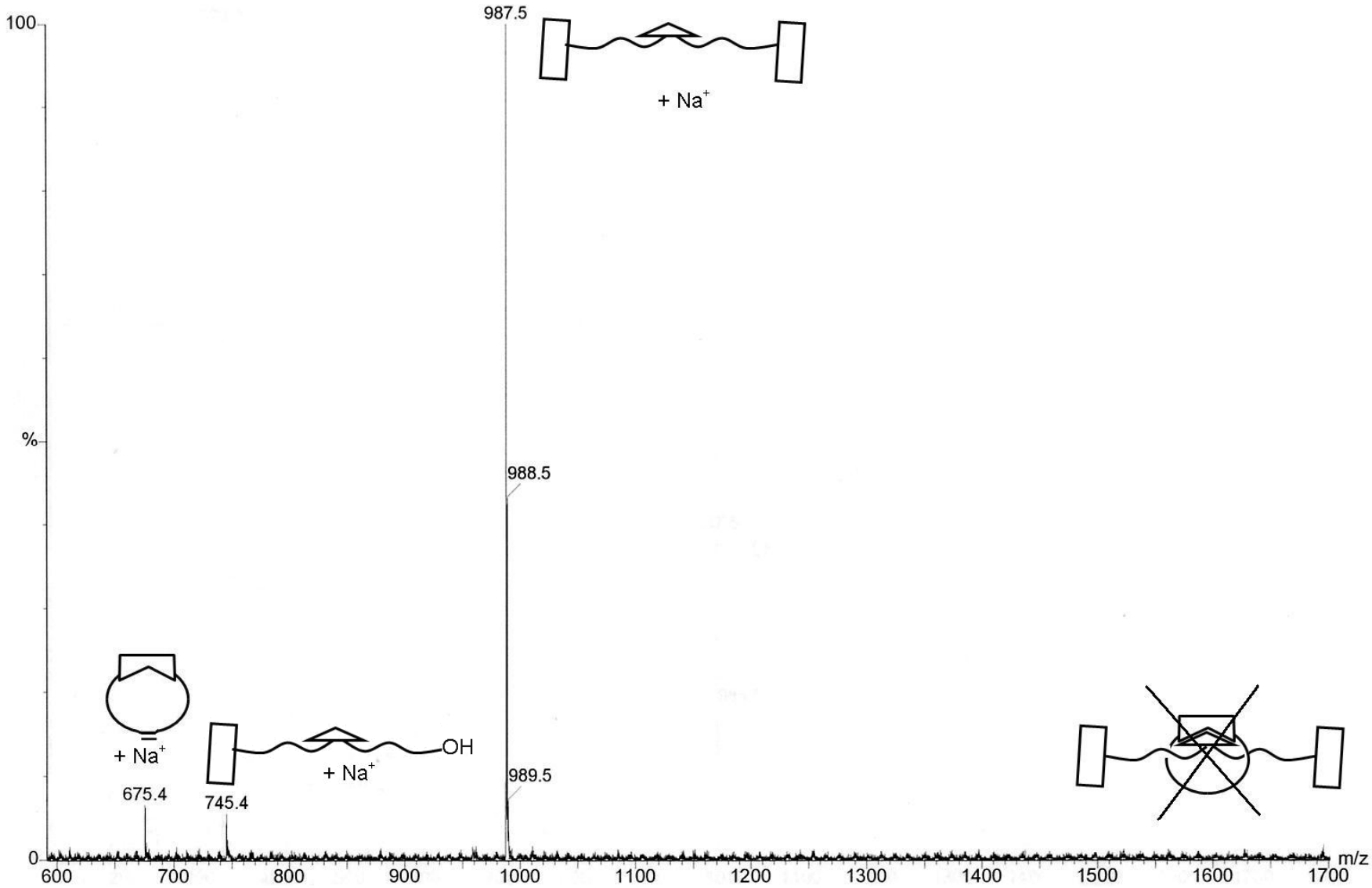
MALDI of 1:1 mixture of **18** and **34**, after irradiation, detail:



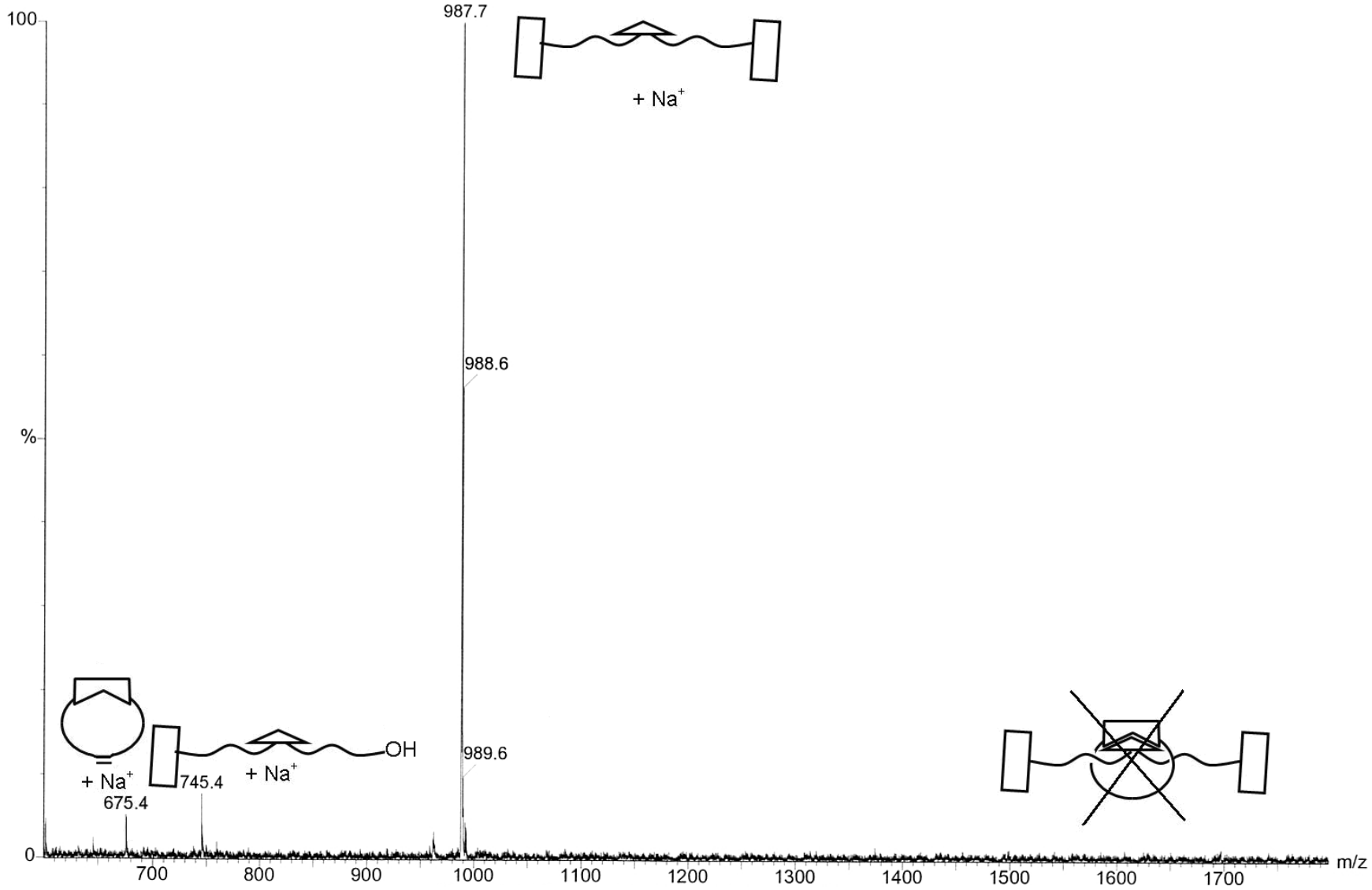
MALDI of 5:1 mixture of **18** and **34**, after irradiation and addition of an excess of barbital, detail:



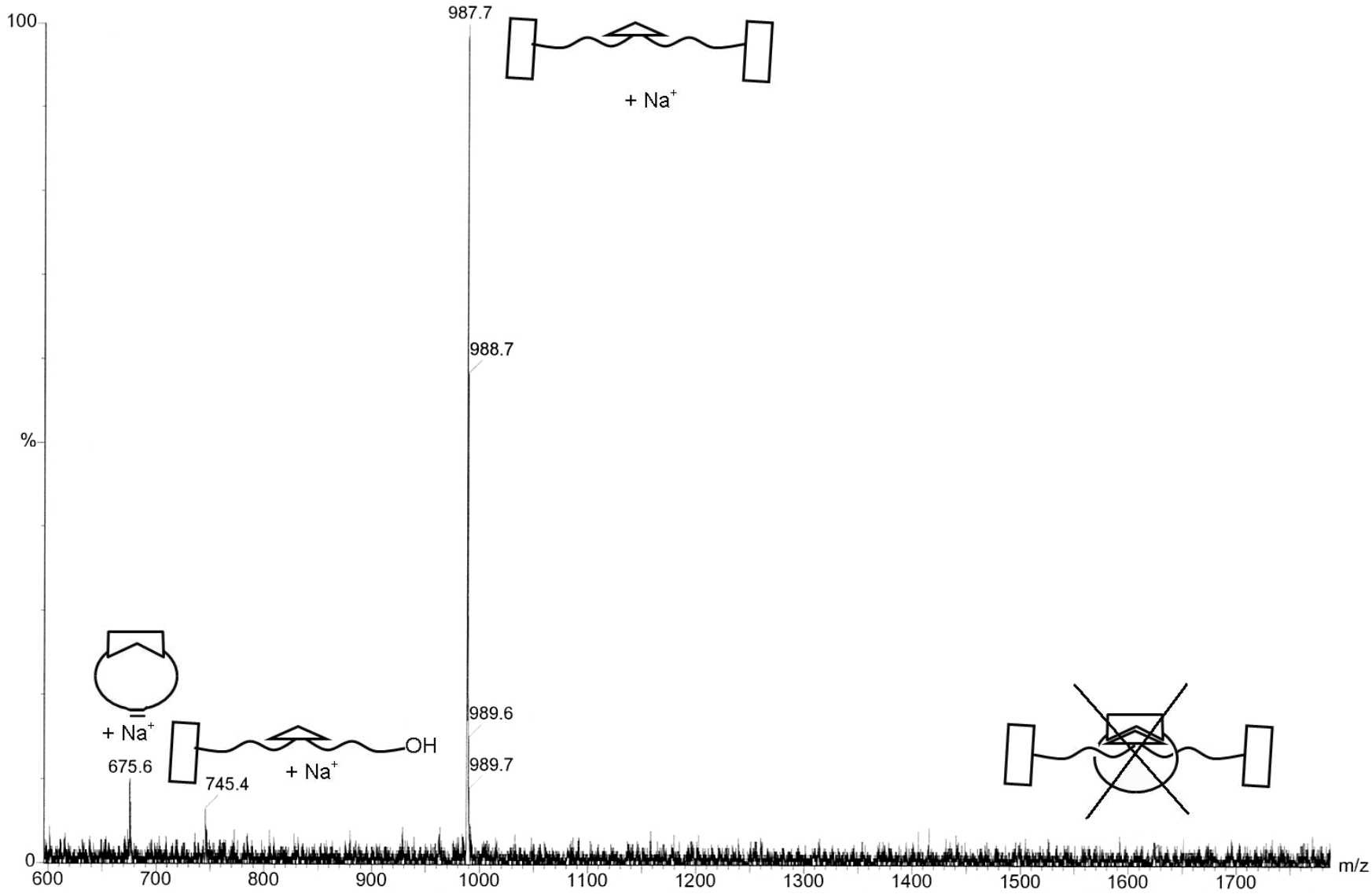
ES$^+$ of 1:1 mixture of **36** and **12** after metathesis, detail:



ES$^+$ of 1:1 mixture of **36** and **15** before metathesis, detail:

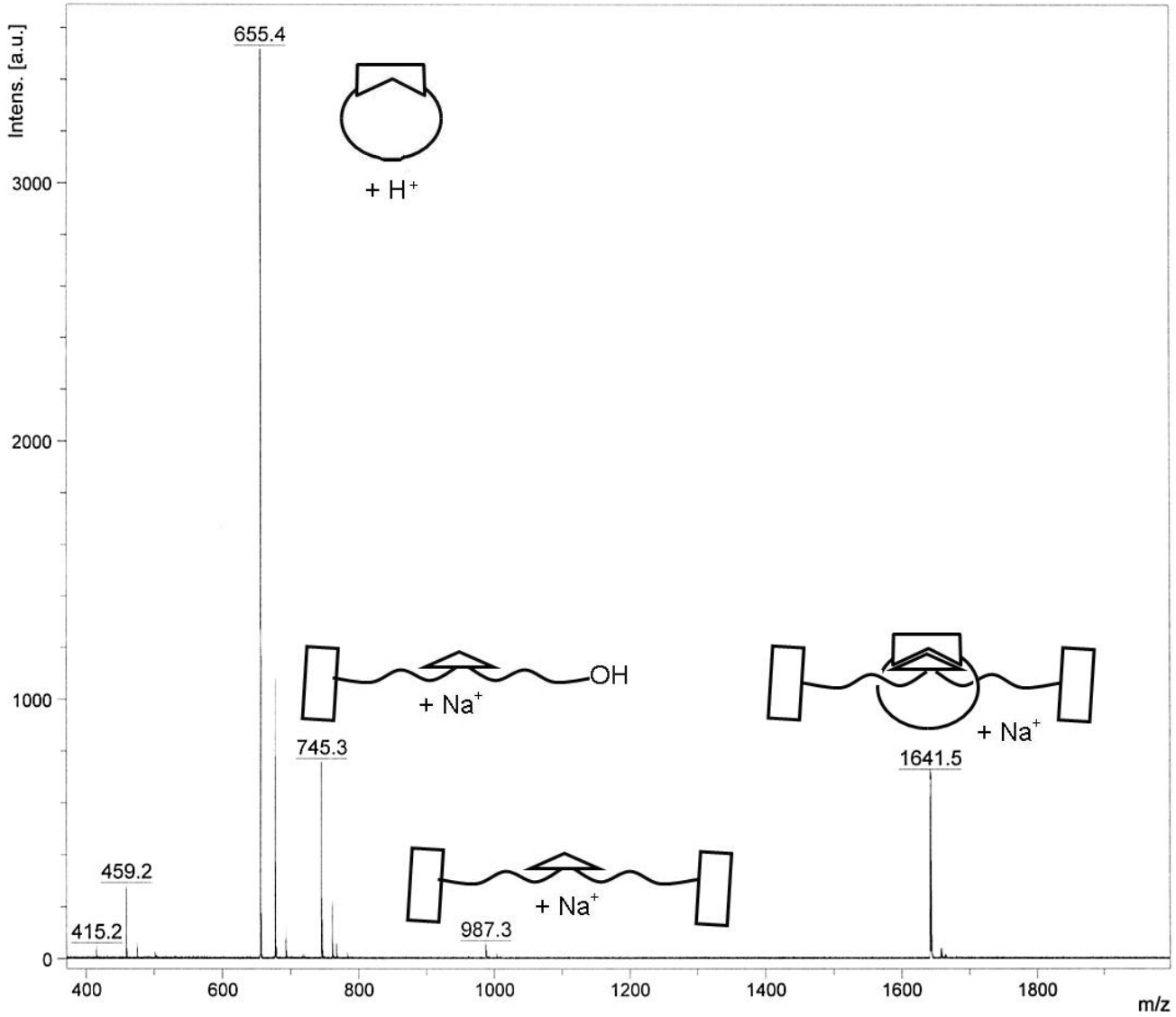


ES$^+$ of 1:1 mixture of **36** and **15** after metathesis, detail:

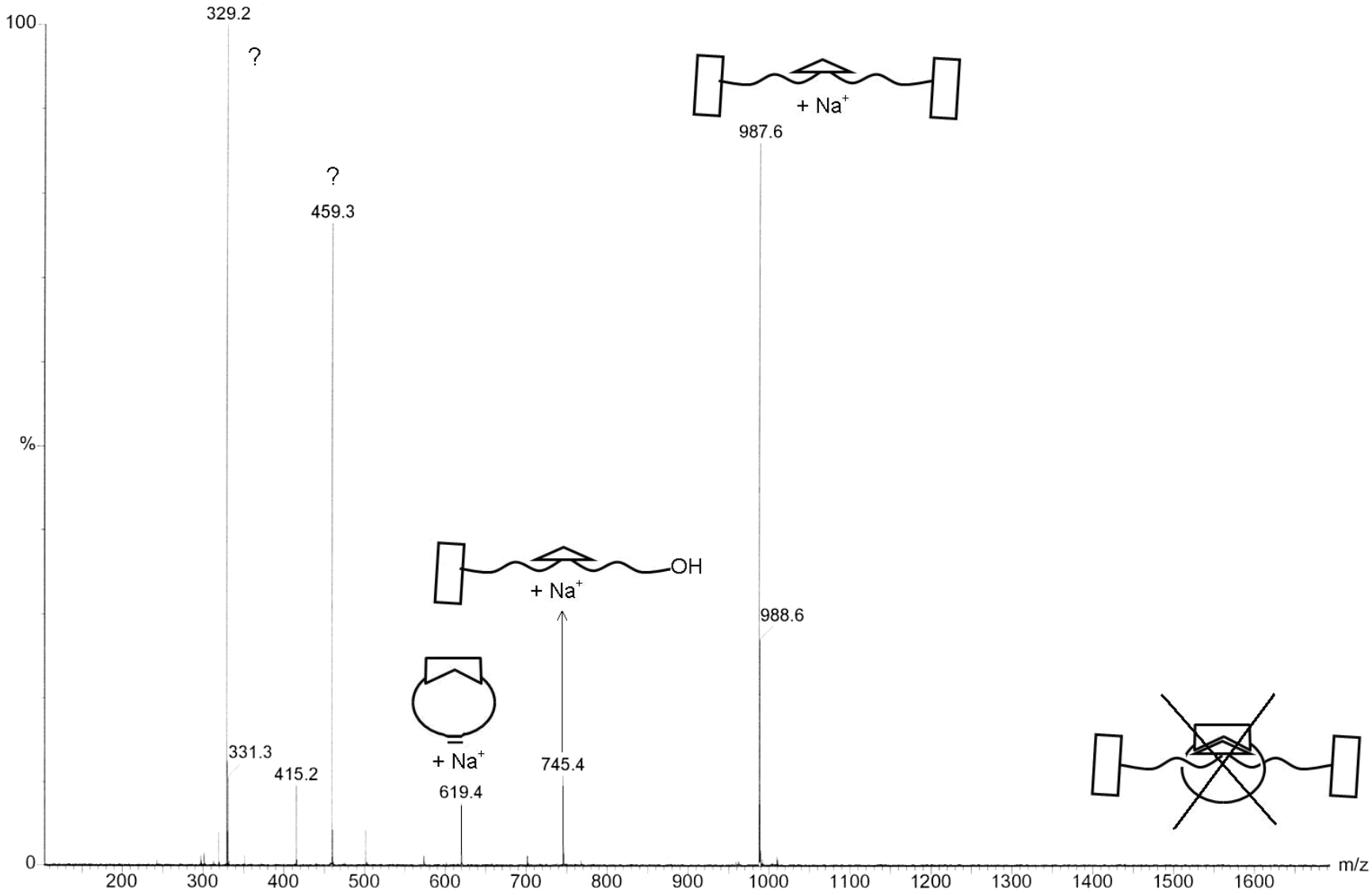


ES$^+$ of 1:1 mixture of **36** and **18**, whole spectrum:

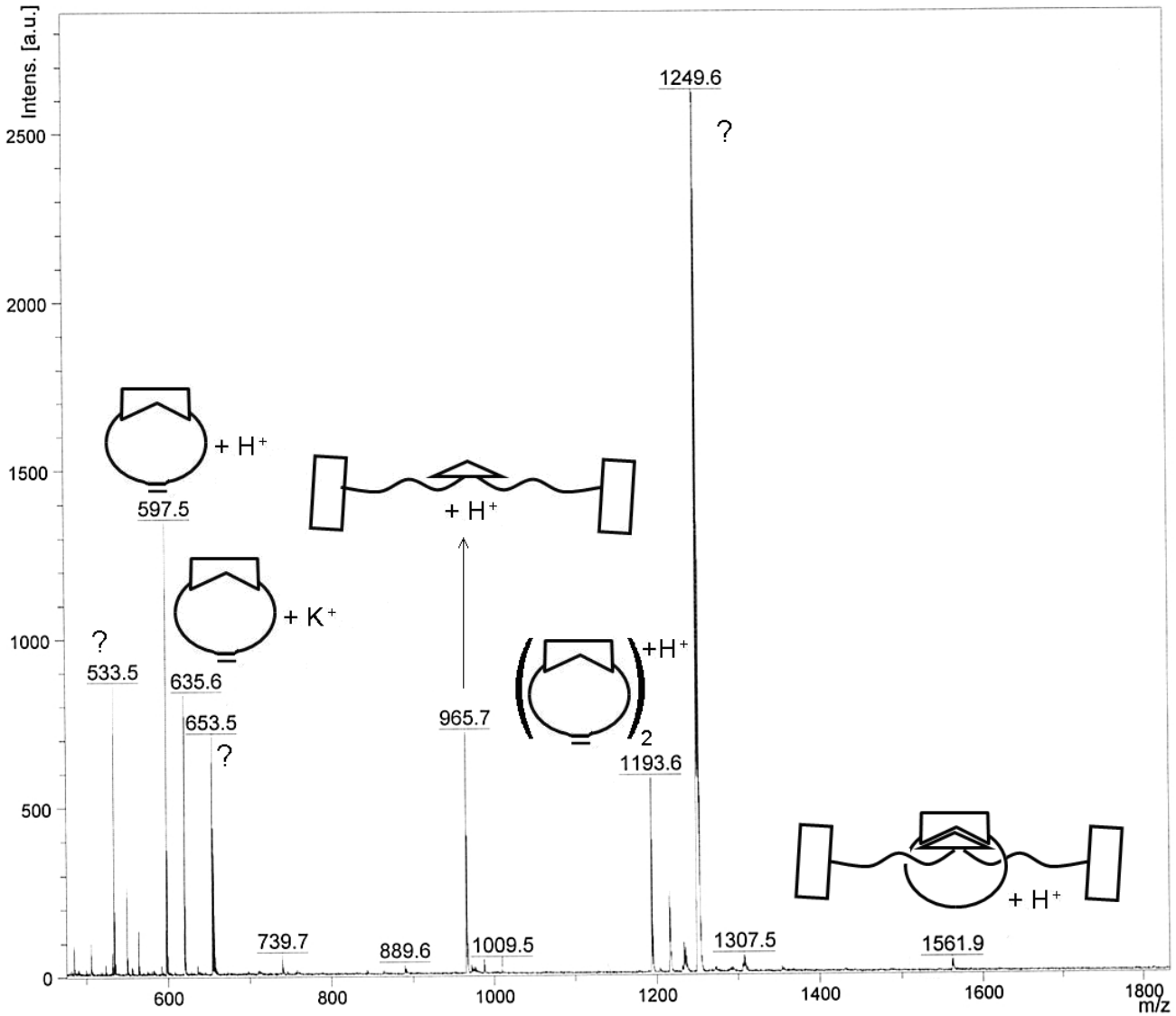
MALDI of 1:1 mixture of **36** and **18**, detail:



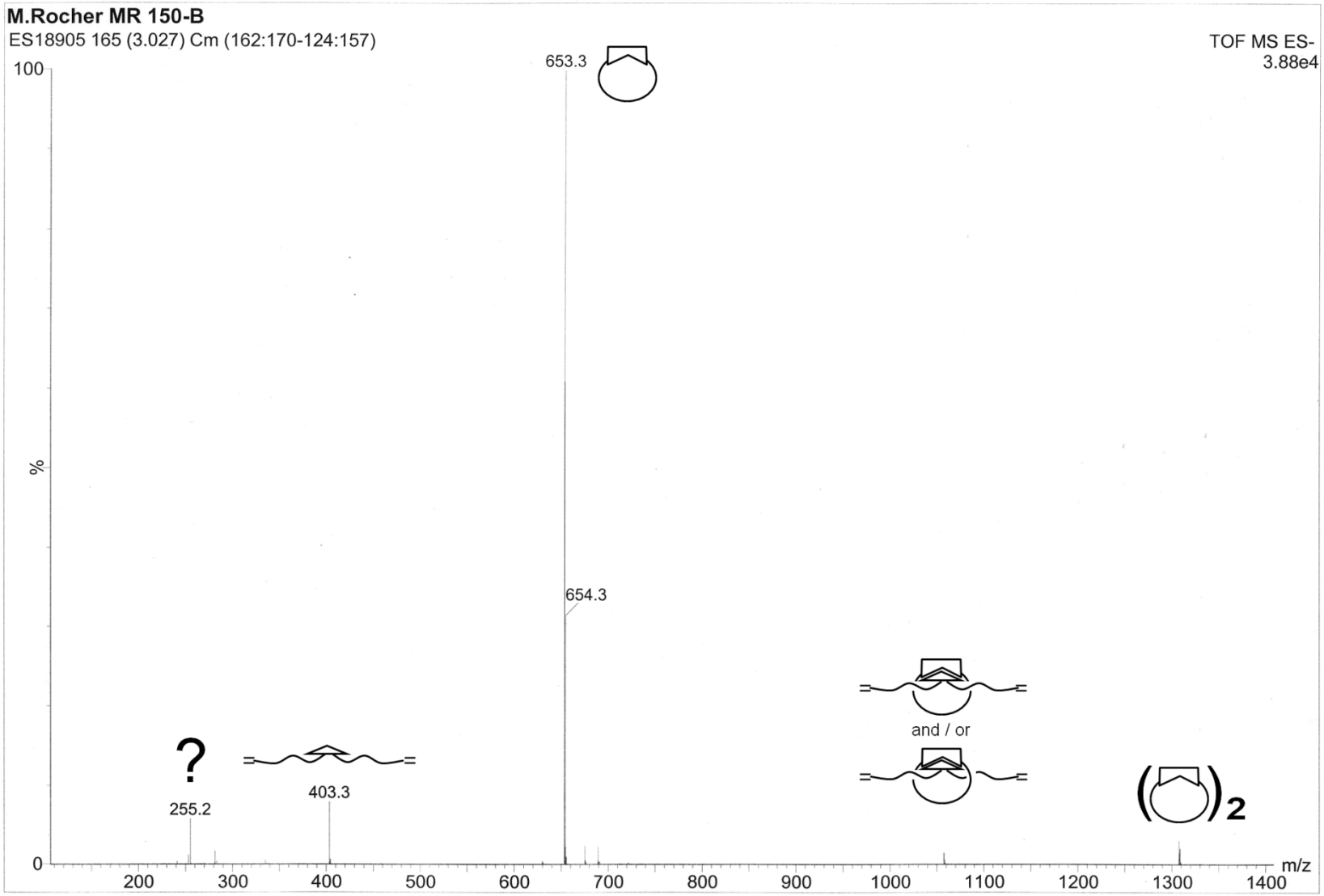
ES$^+$ of 1:1 mixture of **36** and **14** after metathesis, whole spectrum:



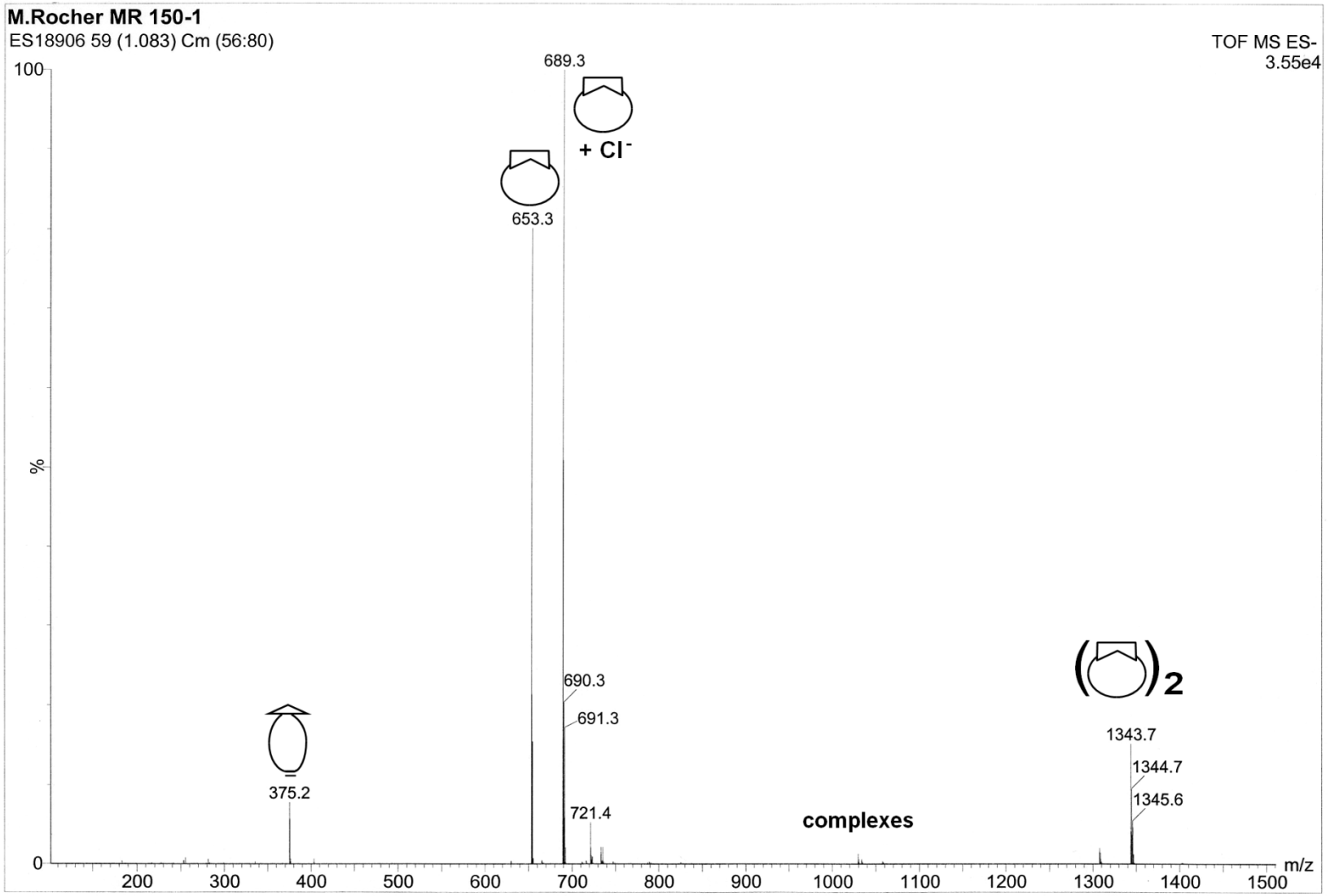
MALDI of 1:1 mixture of **36** and **14** after metathesis, detail:



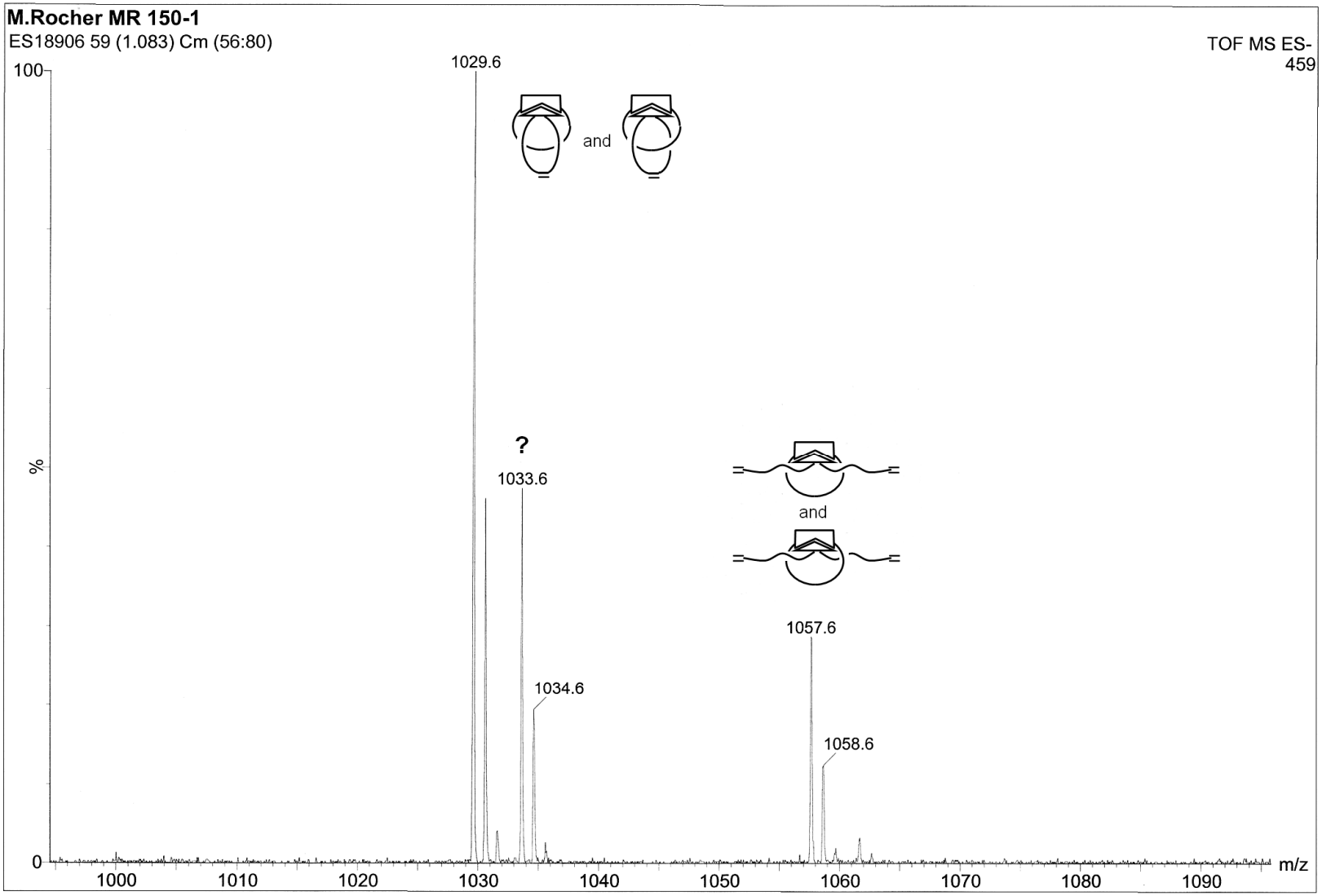
ES$^-$ of 1:1 mixture of **37** and **18**, whole spectrum:



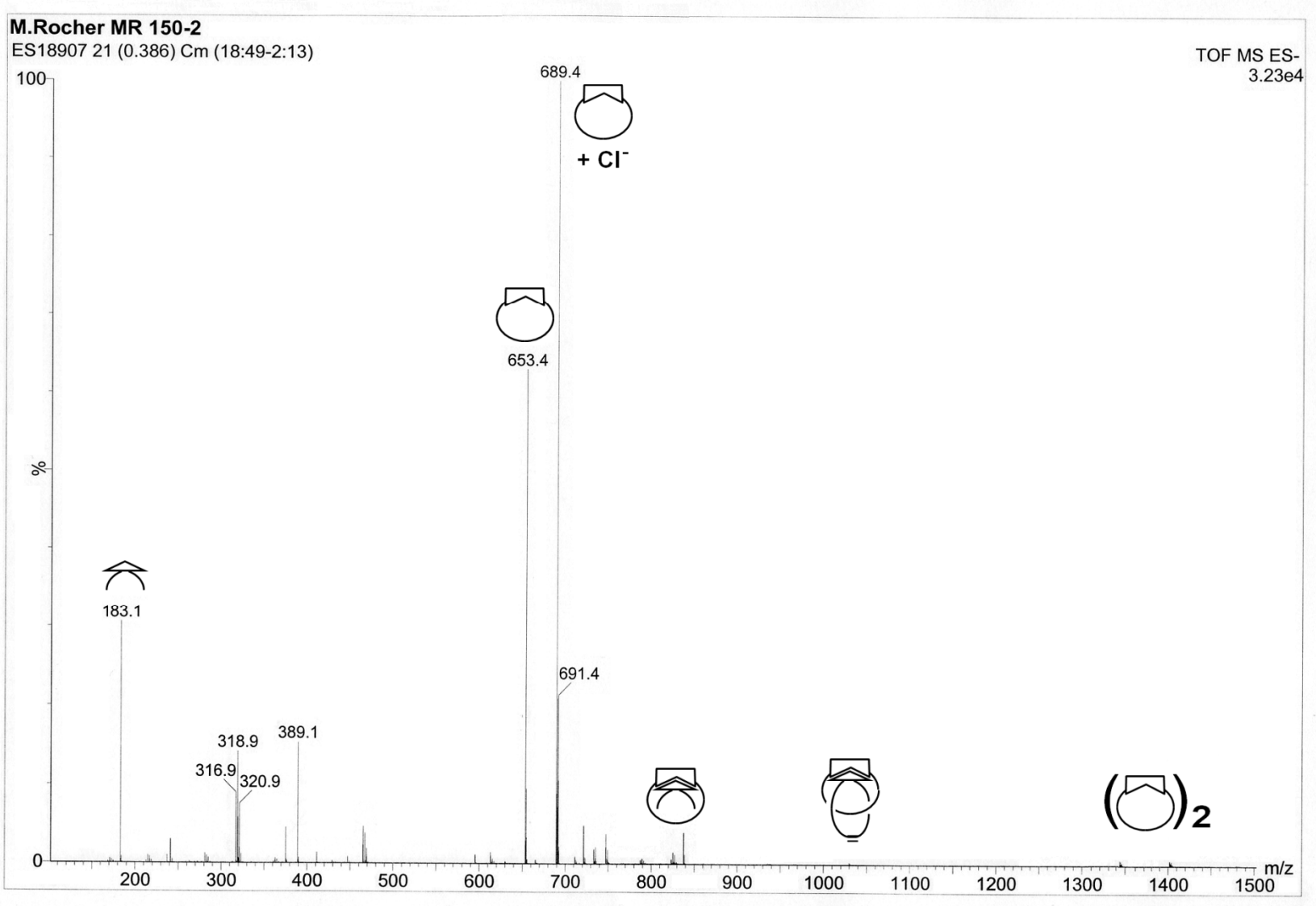
ES$^-$ of 1:1 mixture of **37** and **18** after metathesis, whole spectrum:



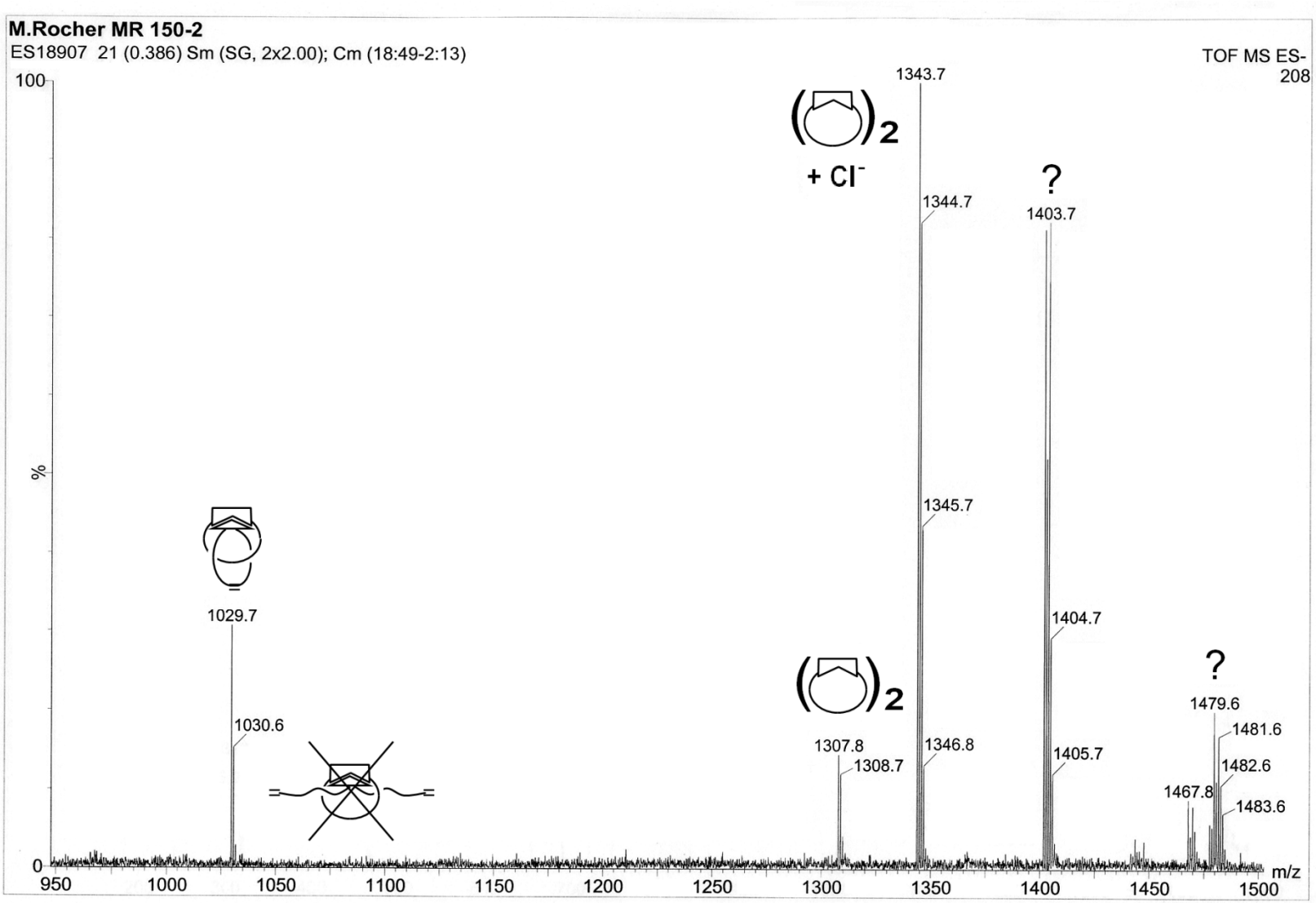
ES$^-$ of 1:1 mixture of **37** and **18** after metathesis, detail:



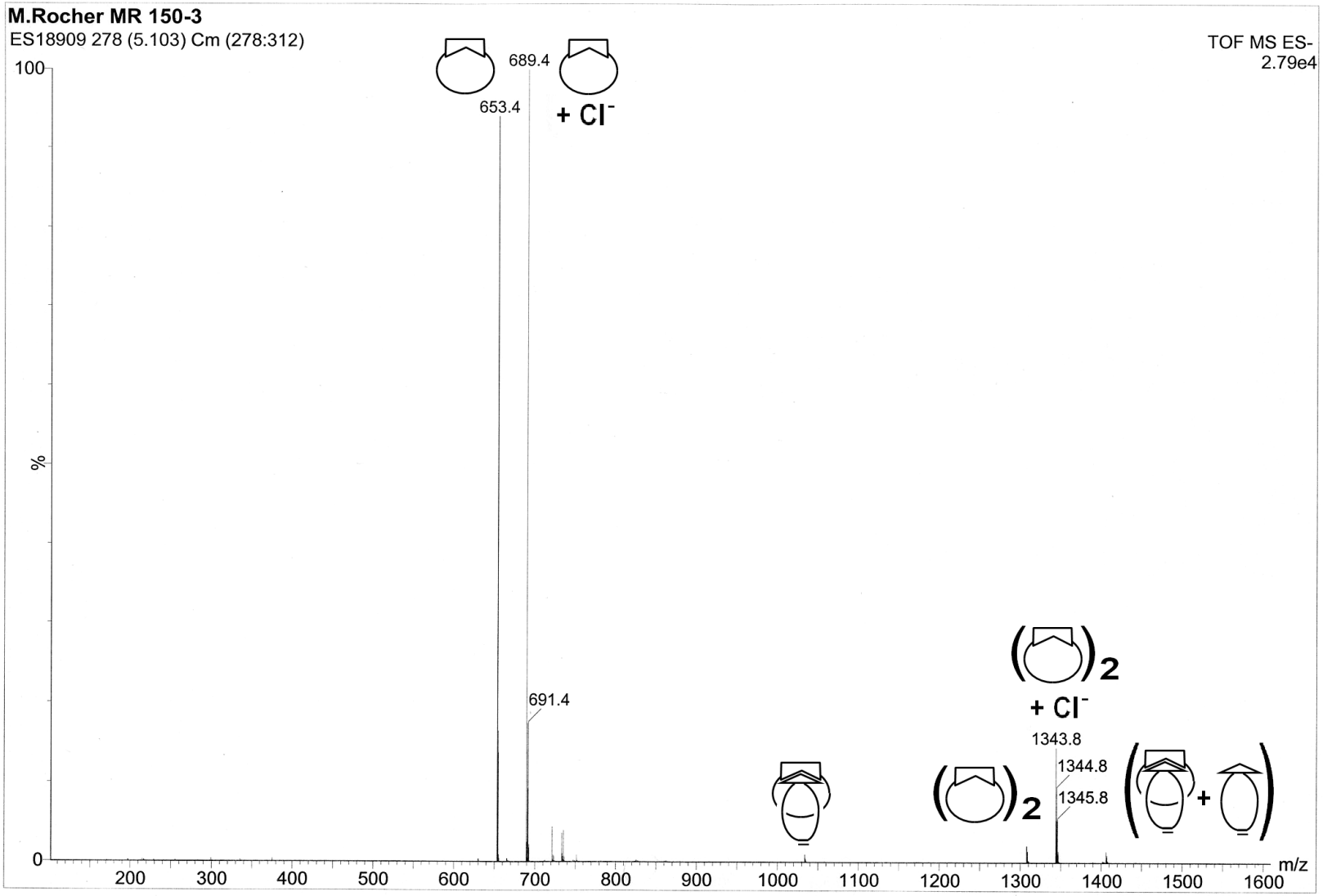
ES$^-$ of 1:1 mixture of **37** and **18** after metathesis, plus excess of barbital, whole spectrum:



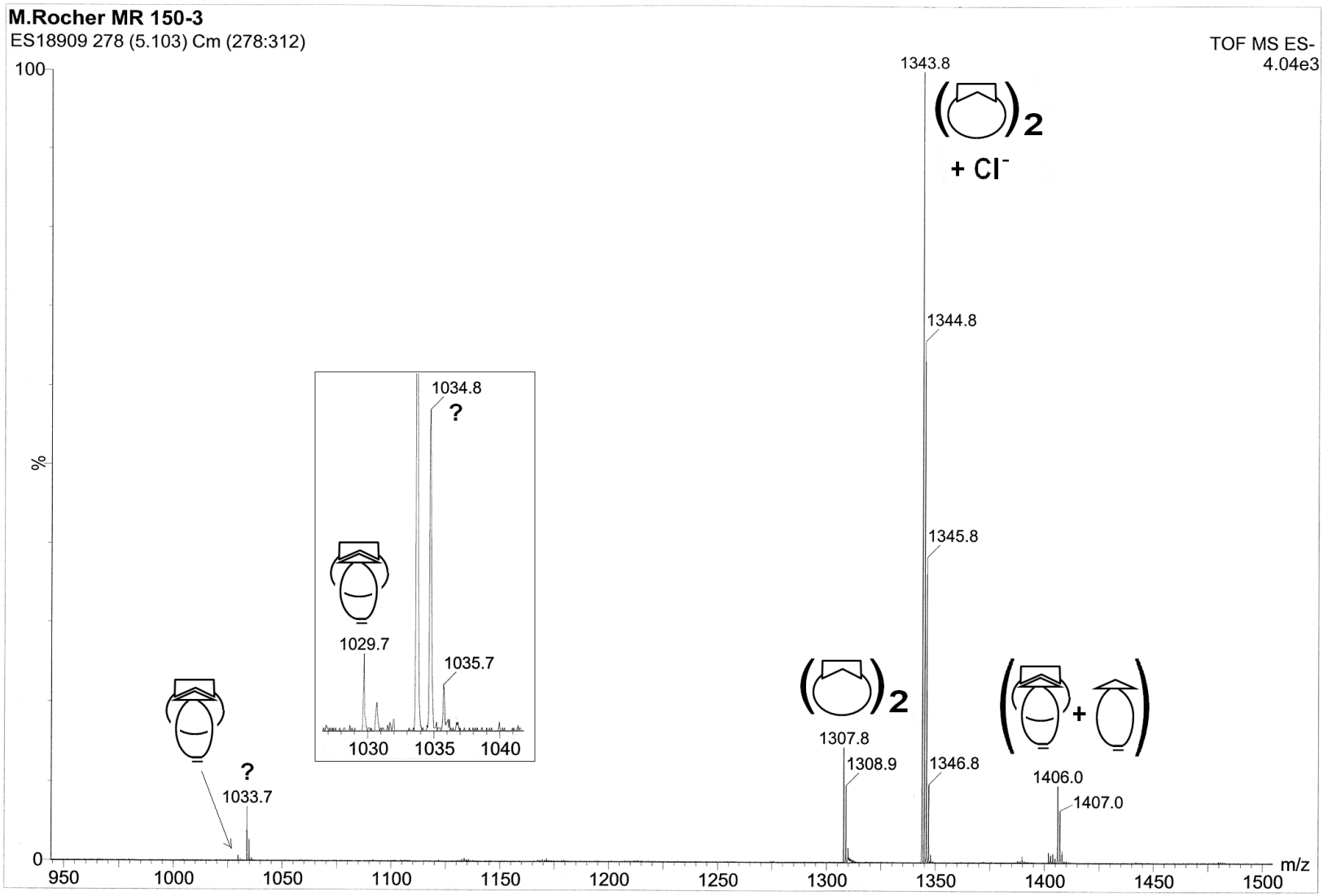
ES$^-$ of 1:1 mixture of **37** and **18** after metathesis, plus excess of barbital, detail:



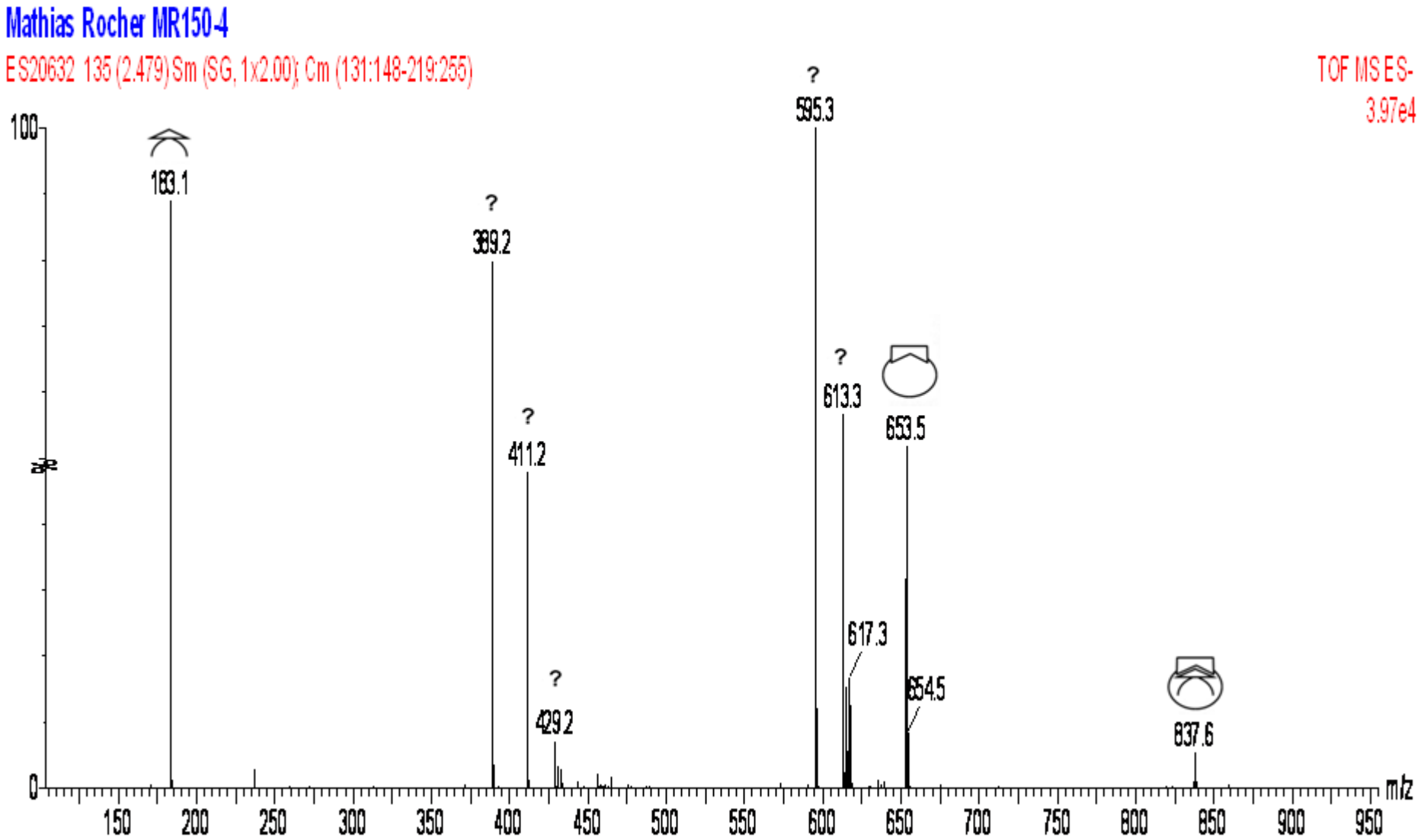
ES$^-$ of 1:1 mixture of **37c** (**37** closed by metathesis) and **18**, whole spectrum:



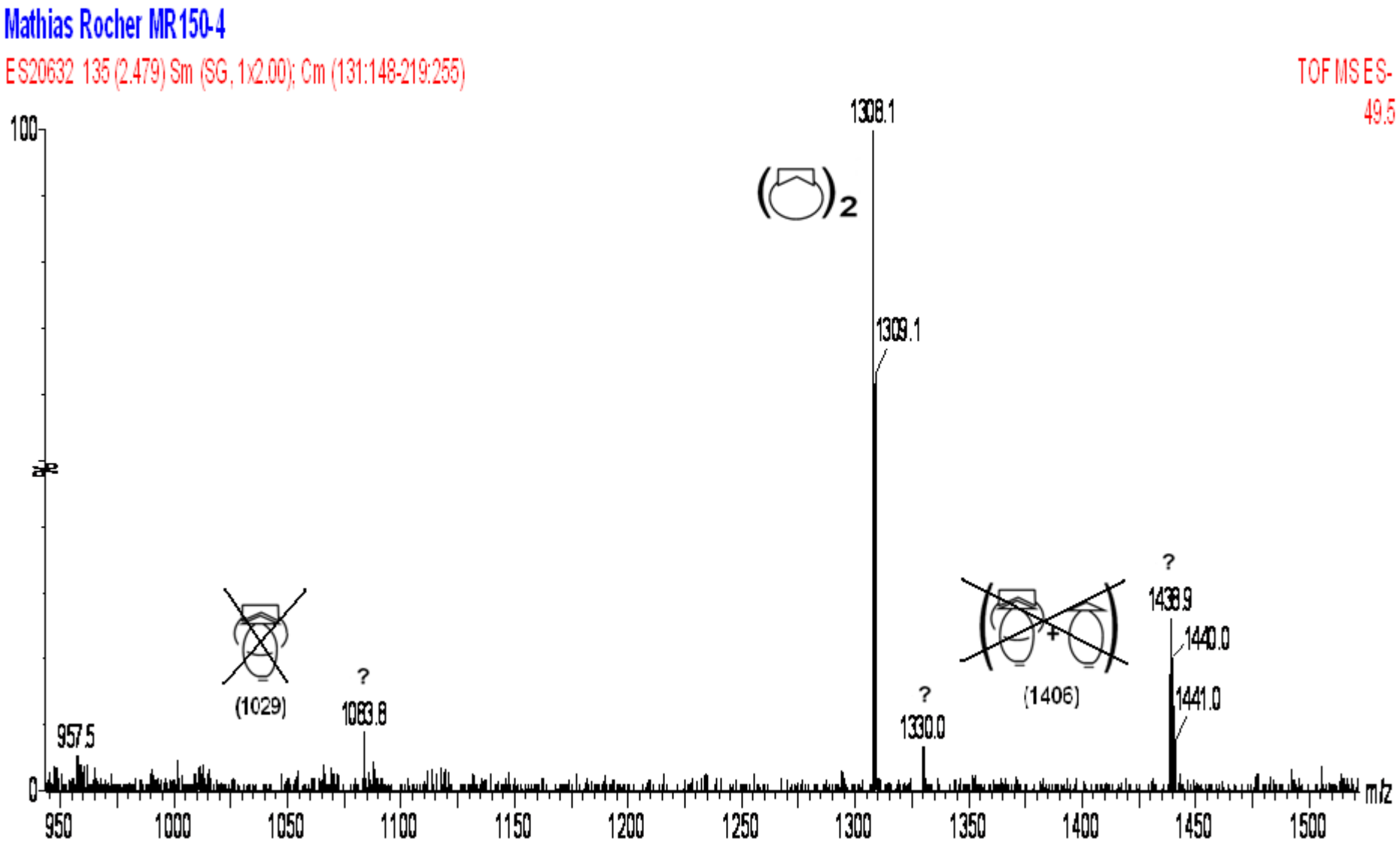
ES$^-$ of 1:1 mixture of **37c** (**37** closed by metathesis) and **18**, detail:



ES$^-$ of 1:1 mixture of **37c** (**37** closed by metathesis) and **18**, plus excess of barbital, spectrum between *0* and *950 Dalton*:



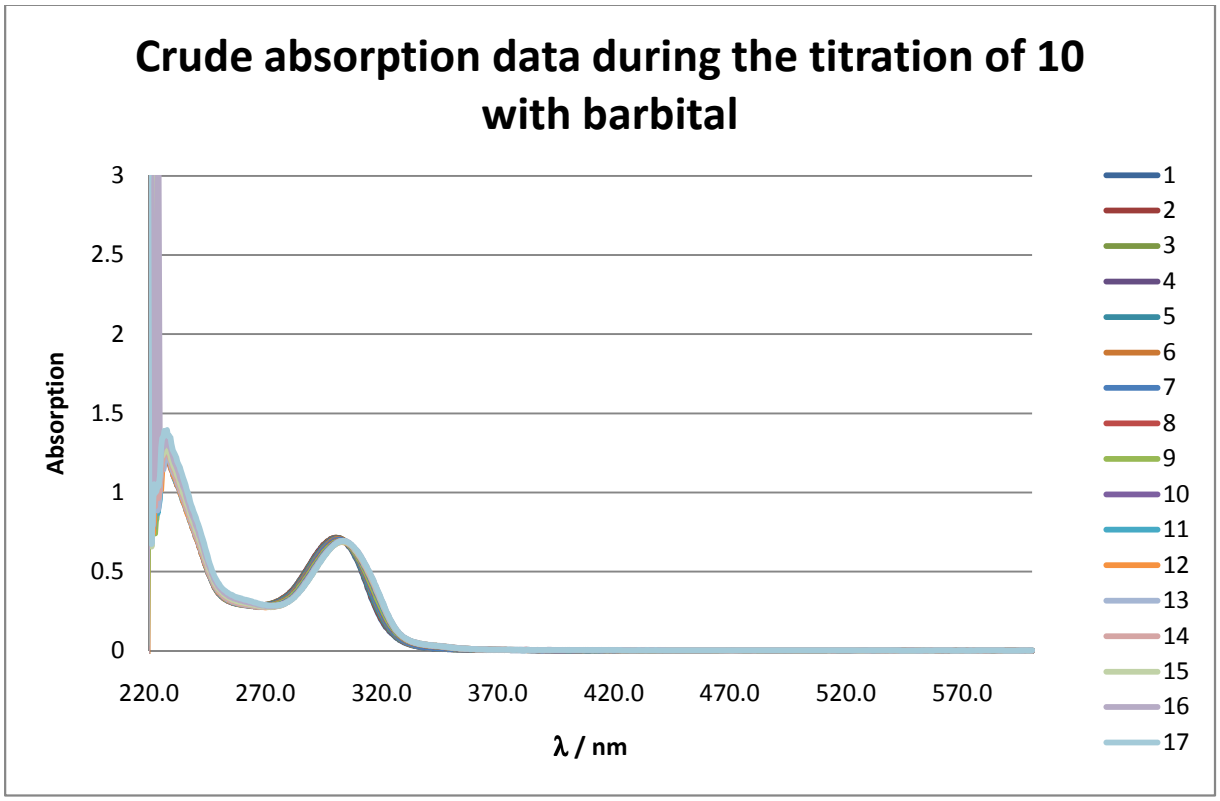
ES$^-$ of 1:1 mixture of **37c** (**37** closed by metathesis) and **18**, plus excess of barbital, spectrum between *950* and *1500 Dalton* (detail):

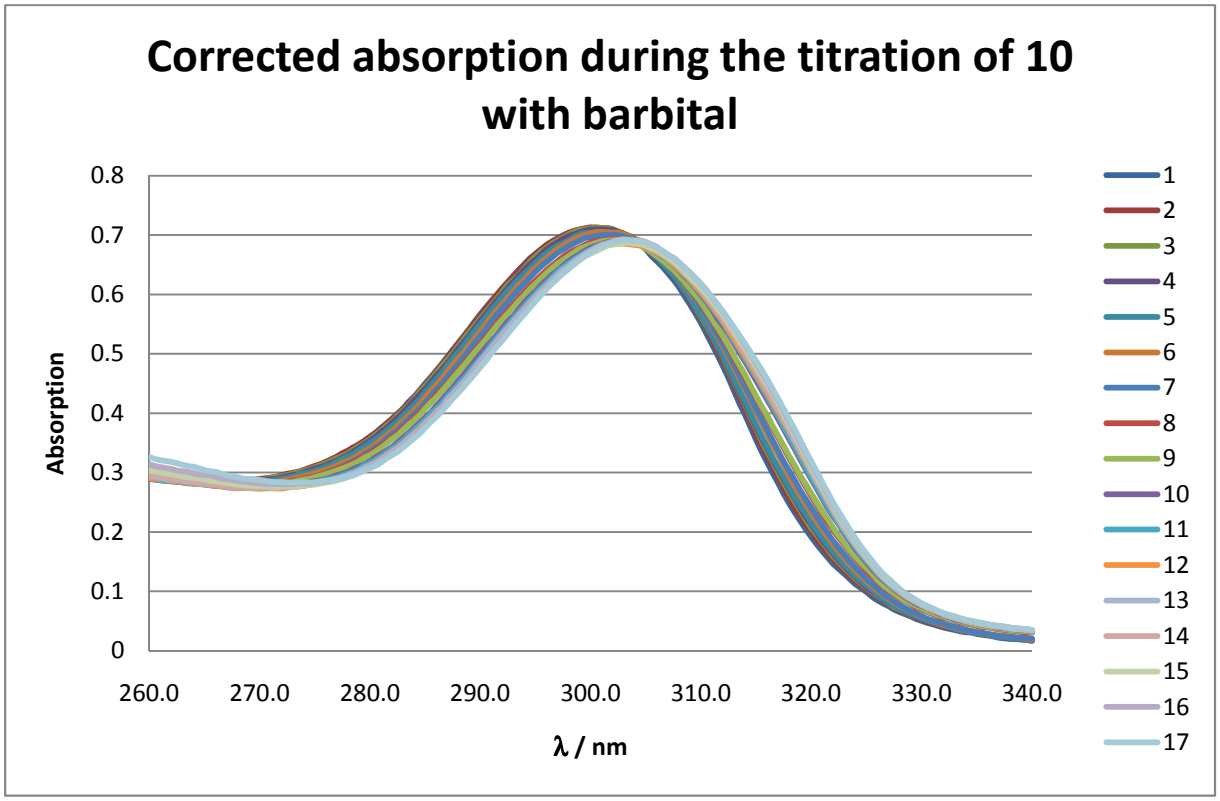


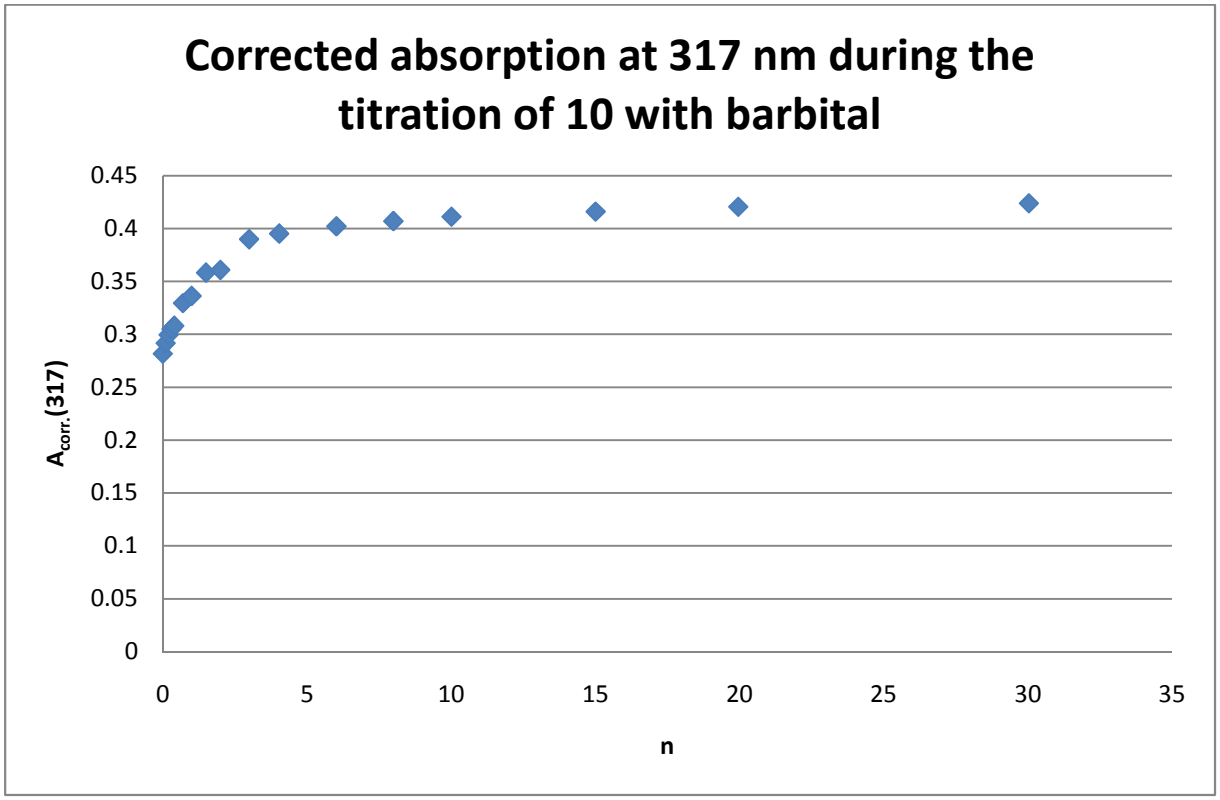
APPENDIX 3

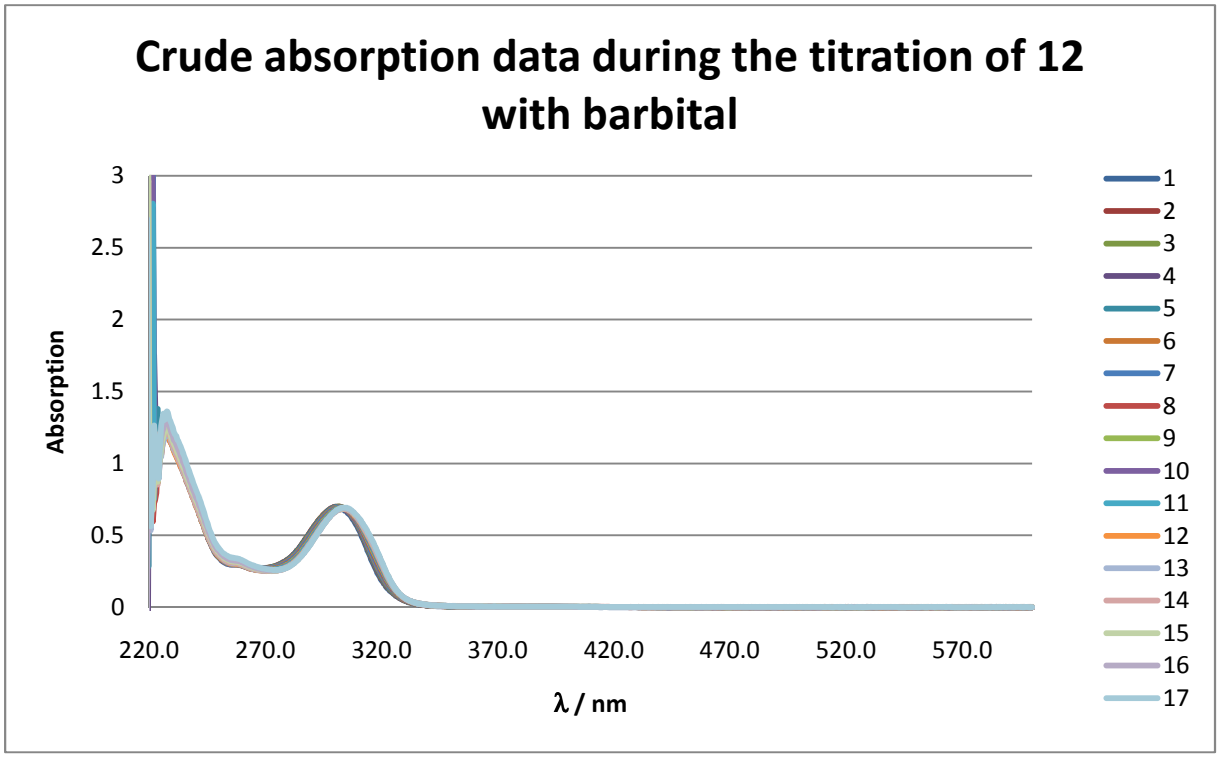
UV and ITC data

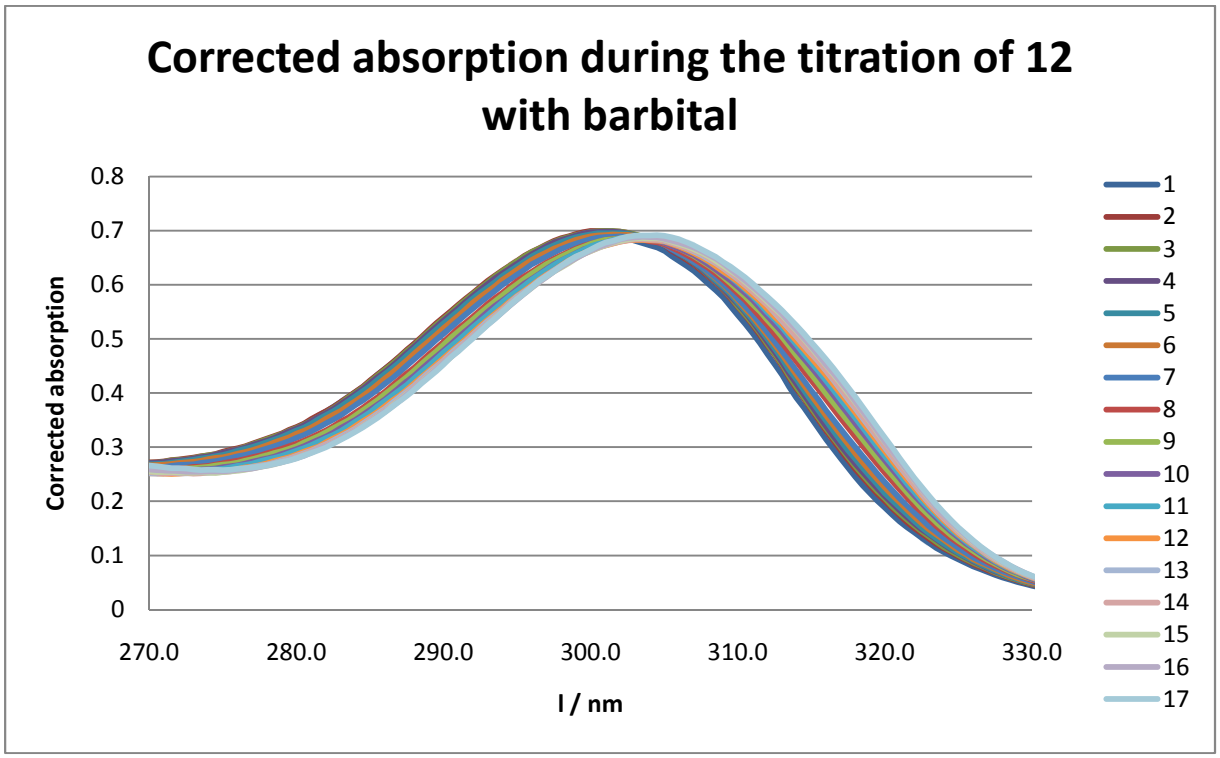
I) UV titration data

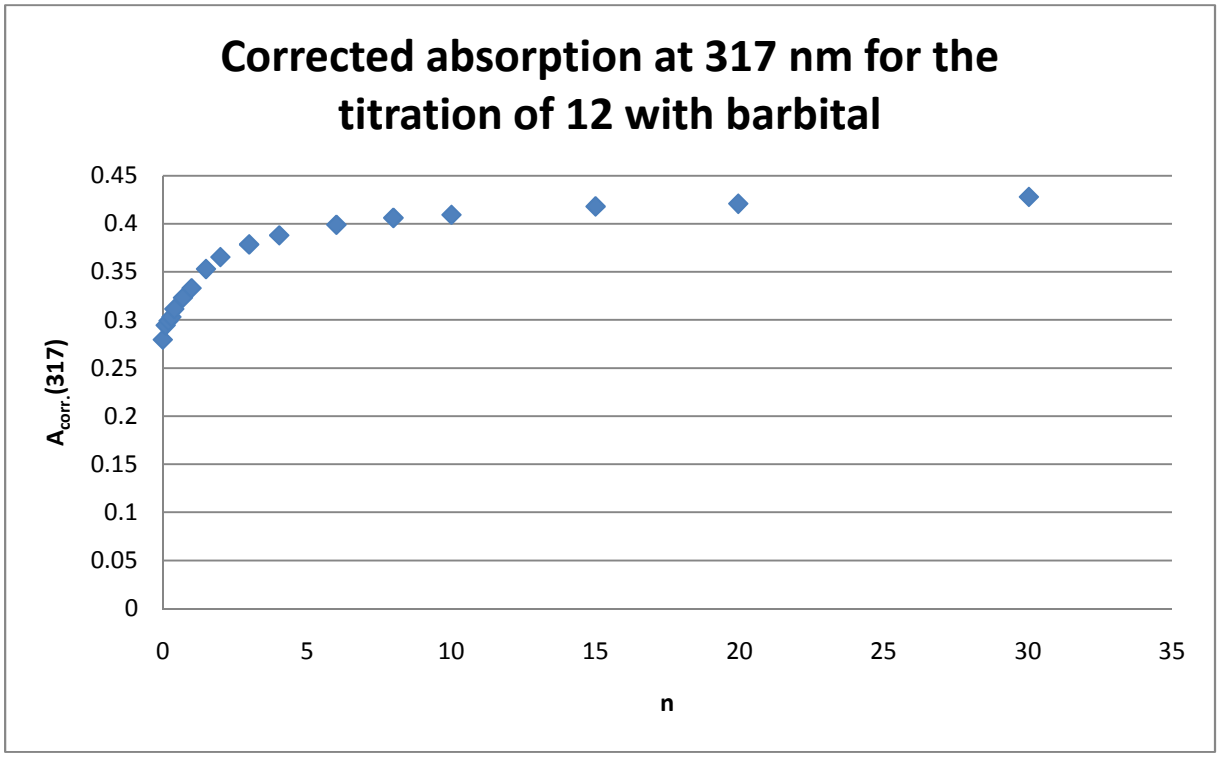


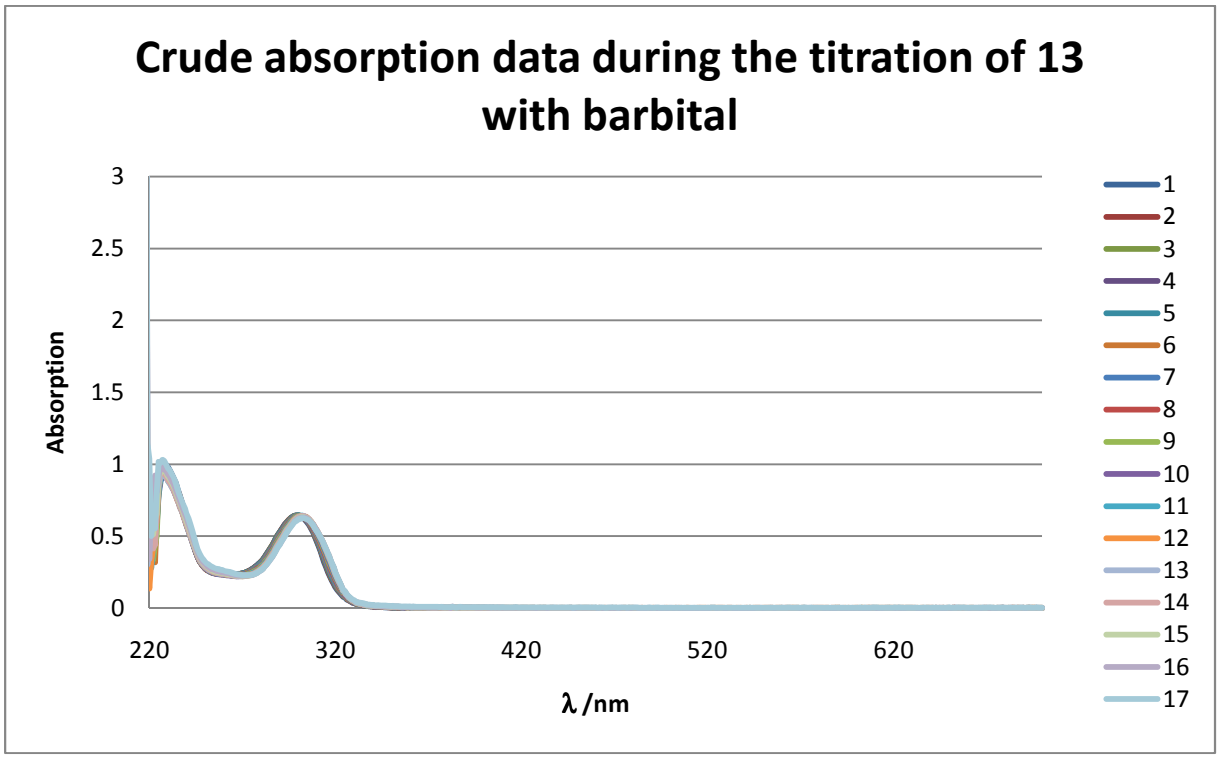

Corrected absorption during the titration of 10 with barbital
Absorption
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
260.0
270.0
280.0
290.0
300.0
310.0
320.0
330.0
340.0
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

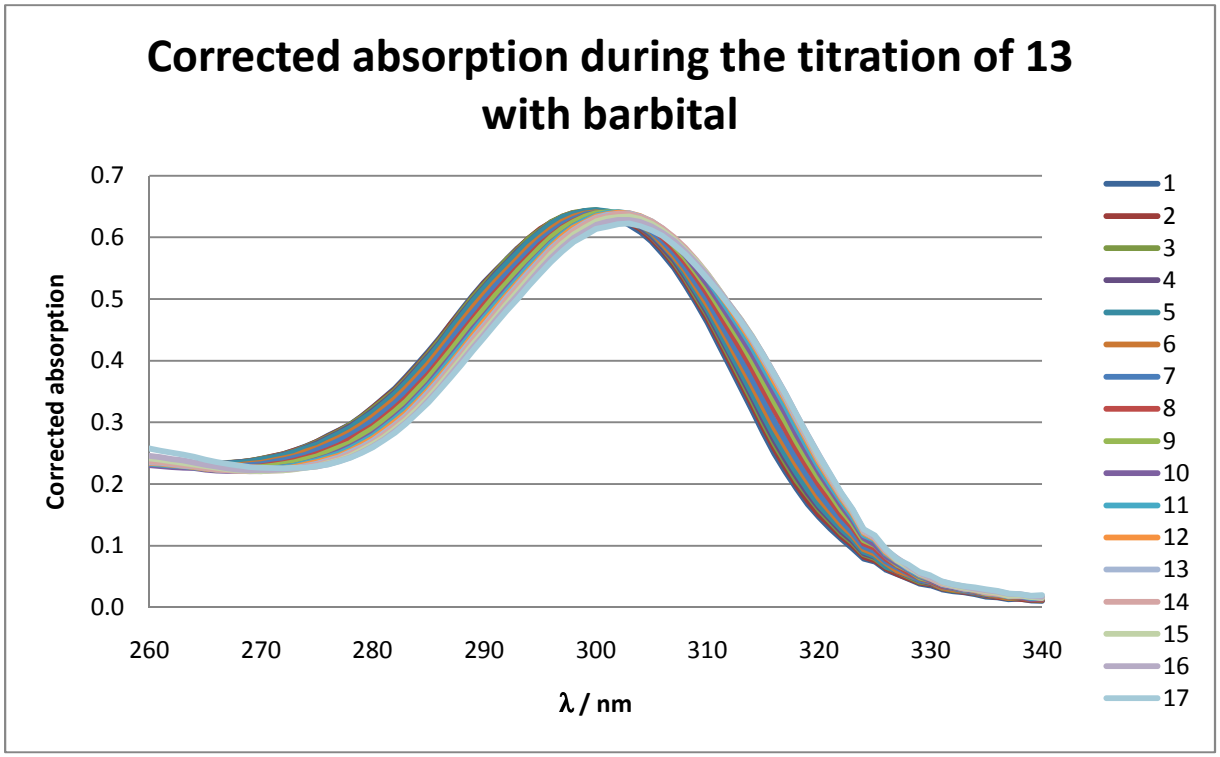

Corrected absorption at 317 nm during the titration of 10 with barbital
A corr.(317)
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15
20
25
30
35
n

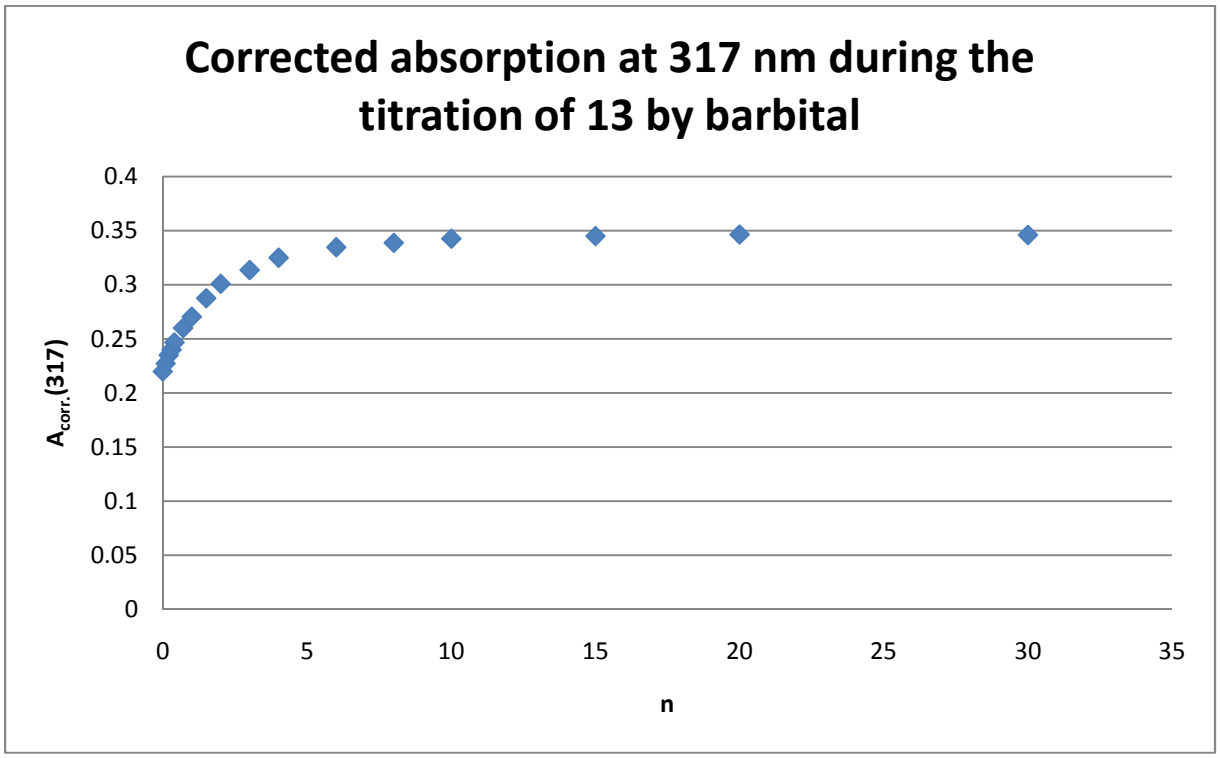

Crude absorption data during the titration of 12 with barbital
Absorption
3
2.5
2
1.5
1
0.5
0
220.0
270.0
320.0
370.0
420.0
470.0
520.0
570.0
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

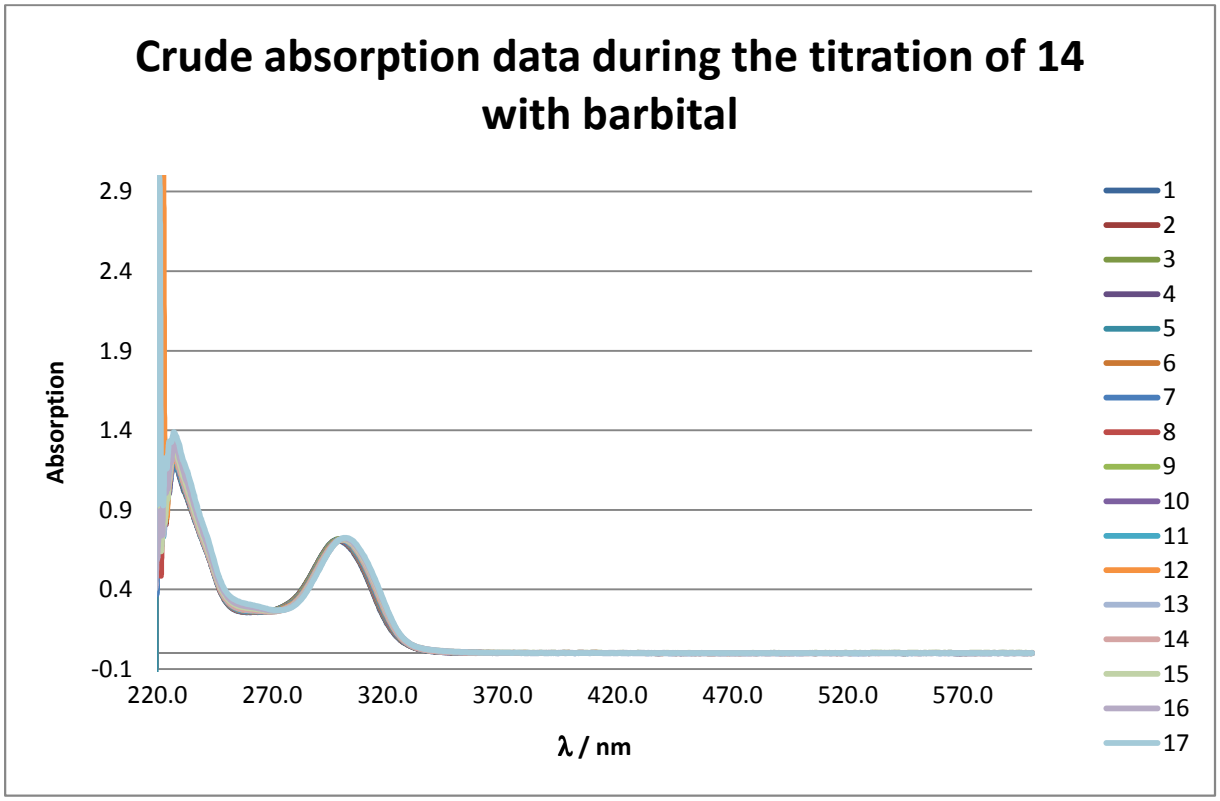

Corrected absorption during the titration of 12 with barbital
Corrected absorption
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
270.0
280.0
290.0
300.0
310.0
320.0
330.0
l / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

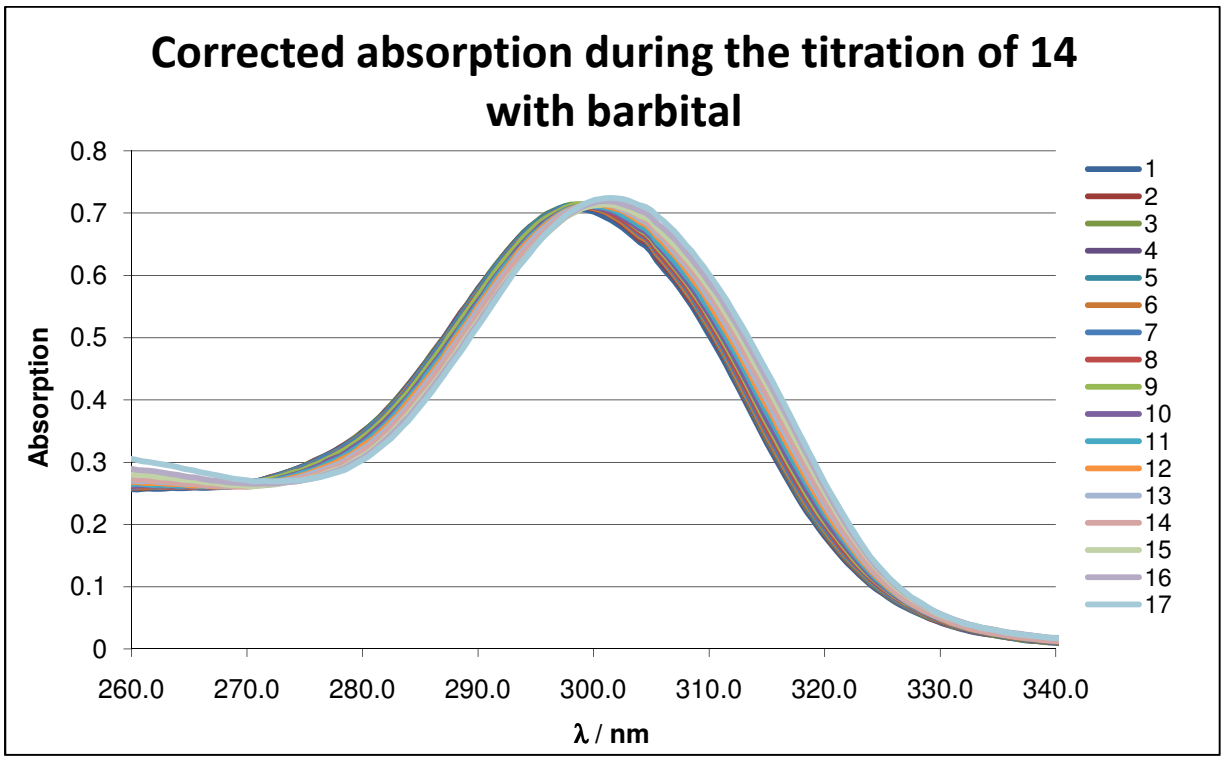

Corrected absorption at 317 nm for the titration of 12 with barbital
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
A corr.(317)
0
5
10
15
20
25
30
35
n

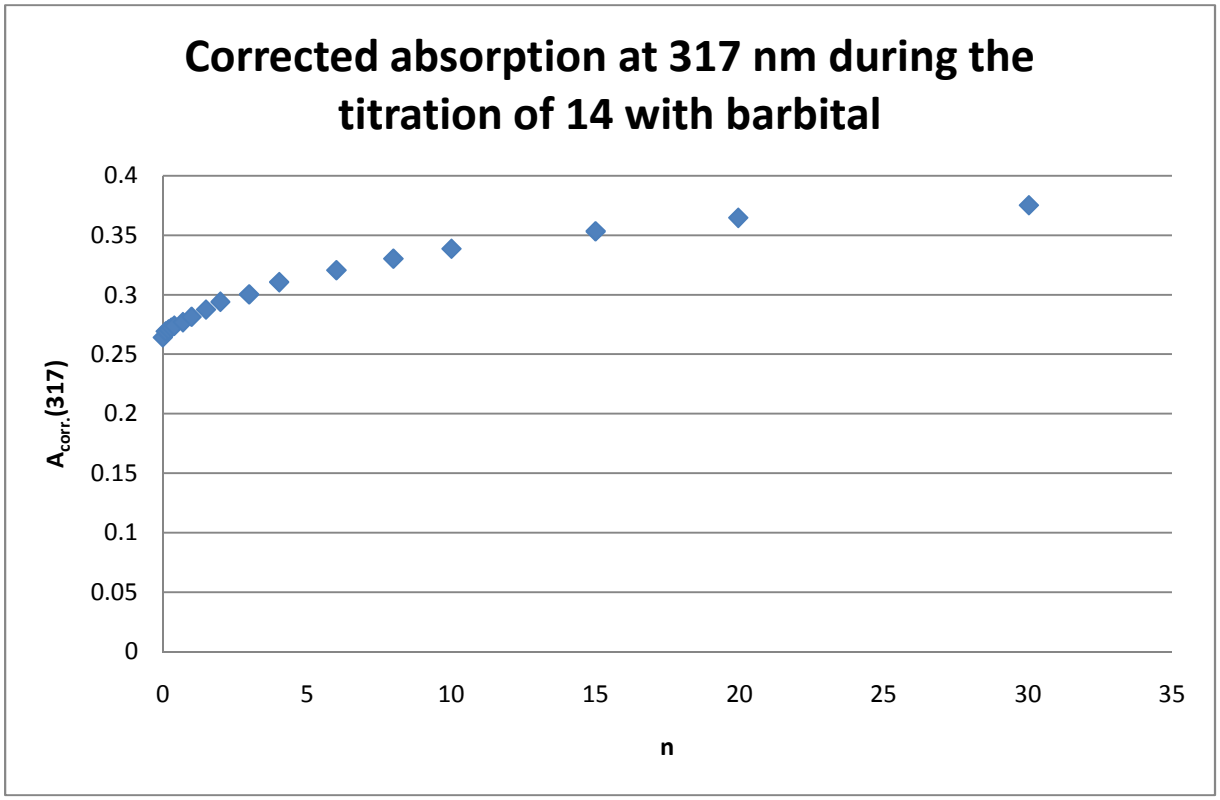

Crude absorption data during the titration of 13 with barbital
3
2.5
2
1.5
1
0.5
0
Absorption
220
320
420
520
620
λ /nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

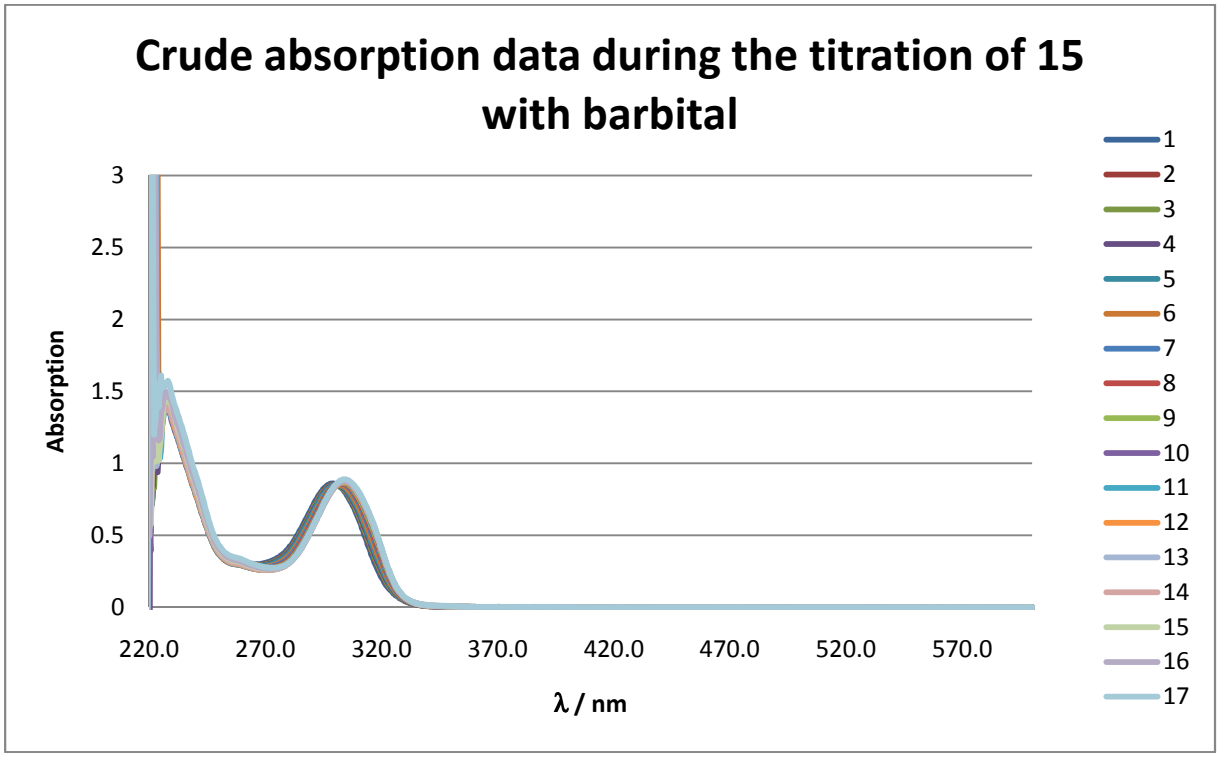

Corrected absorption during the titration of 13 with barbital
Corrected absorption
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
260
270
280
290
300
310
320
330
340
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

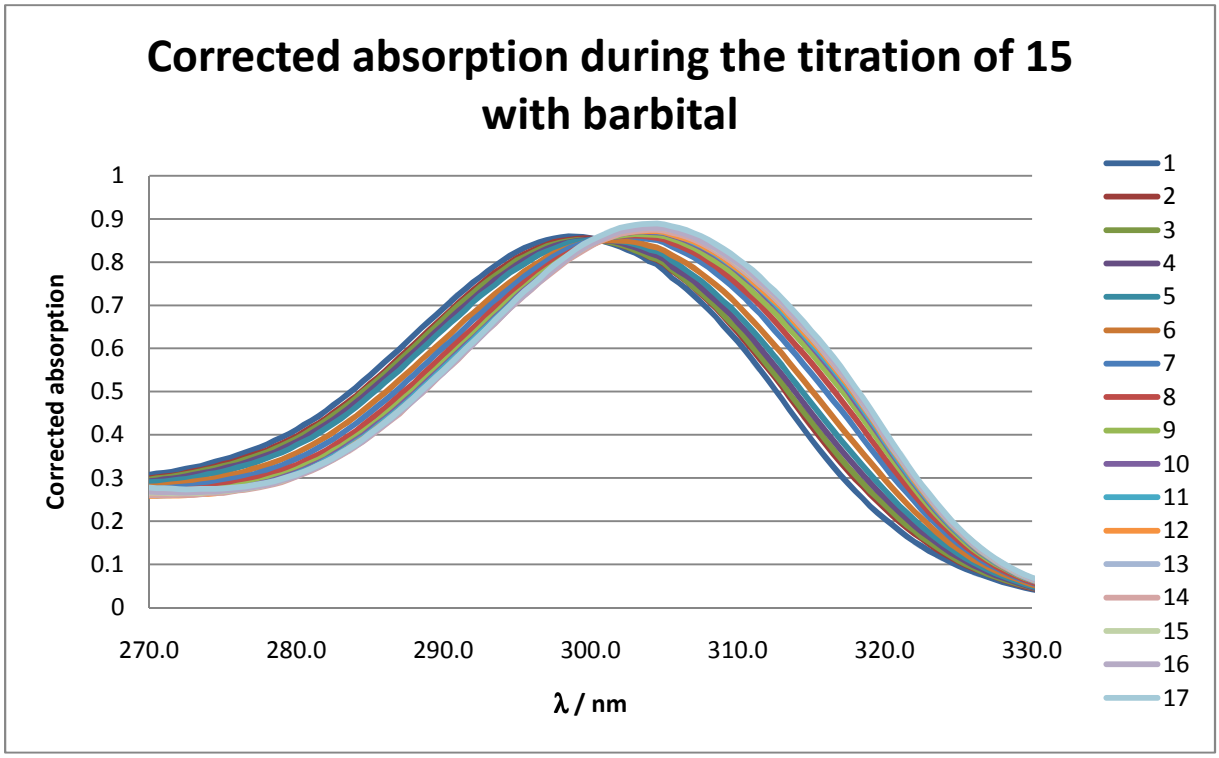

Corrected absorption at 317 nm during the titration of 13 by barbital
$A_{corr.}(317)$
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15
20
25
30
35
n

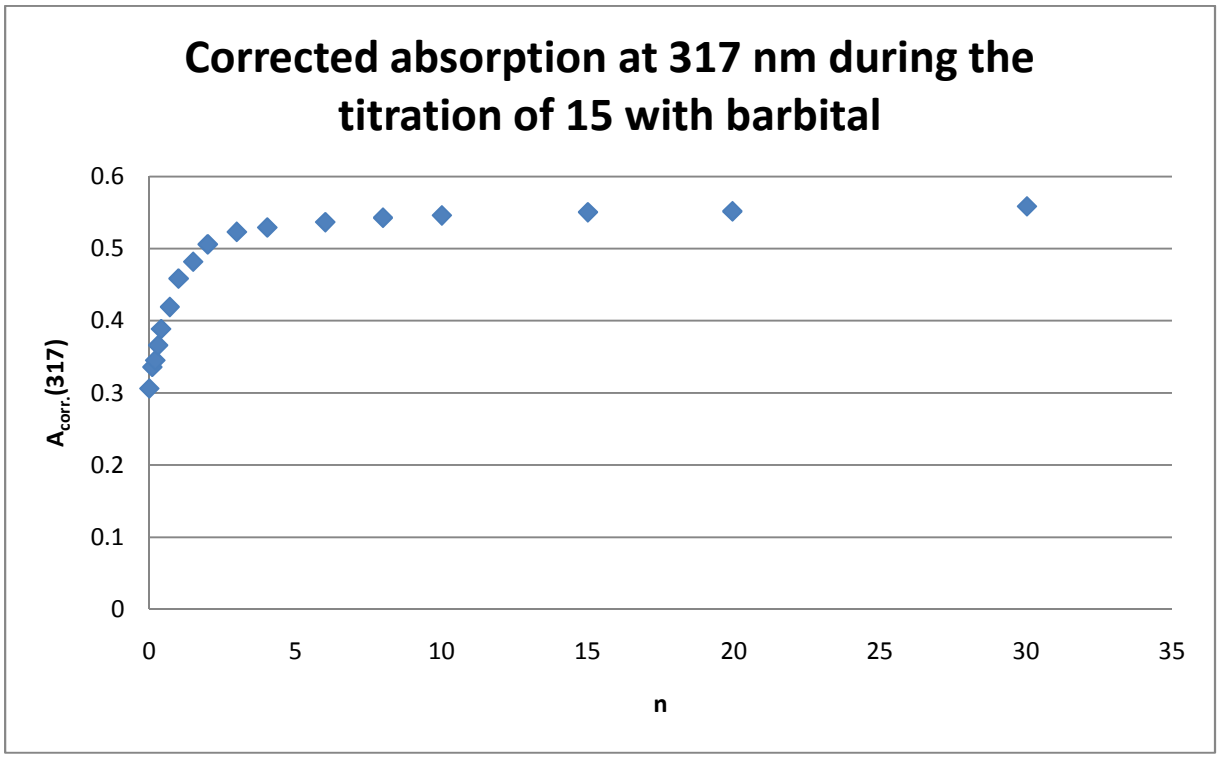

Crude absorption data during the titration of 14 with barbital
Absorption
2.9
2.4
1.9
1.4
0.9
0.4
-0.1
220.0
270.0
320.0
370.0
420.0
470.0
520.0
570.0
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

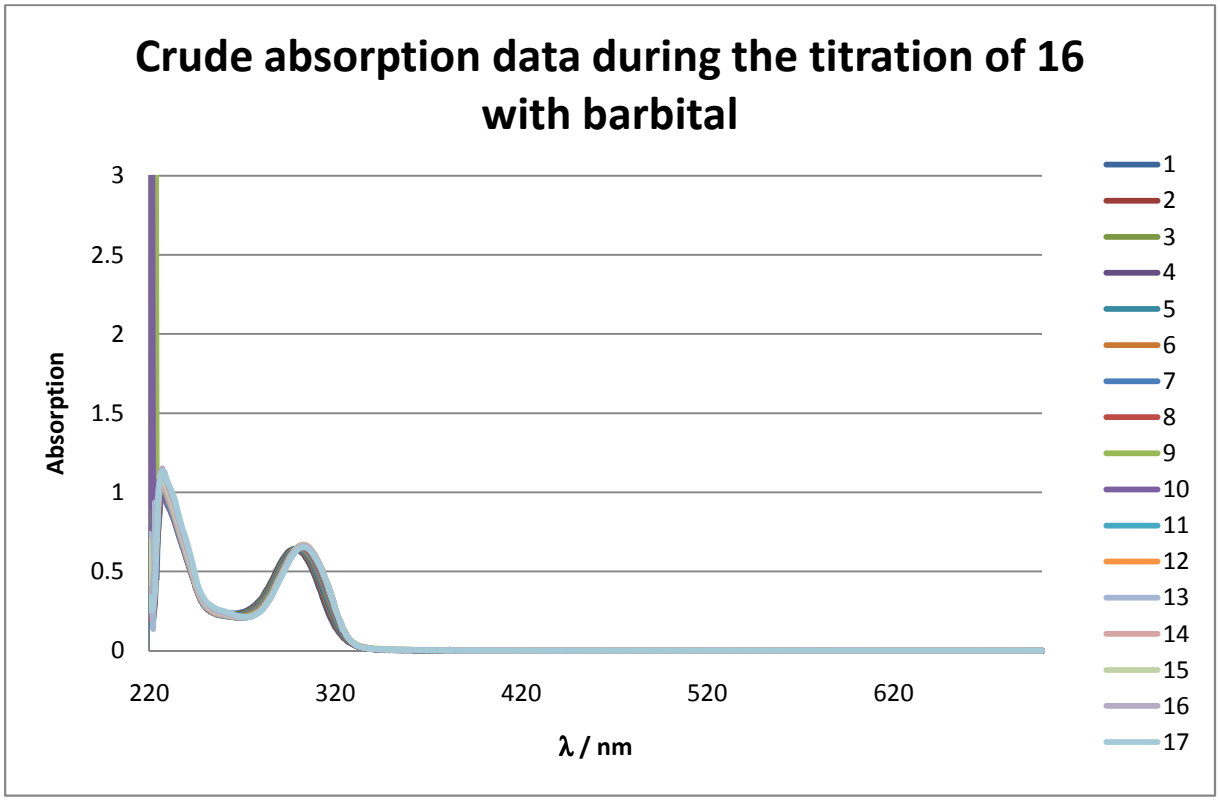

Corrected absorption during the titration of 14 with barbital
Absorption
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
260.0
270.0
280.0
290.0
300.0
310.0
320.0
330.0
340.0
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

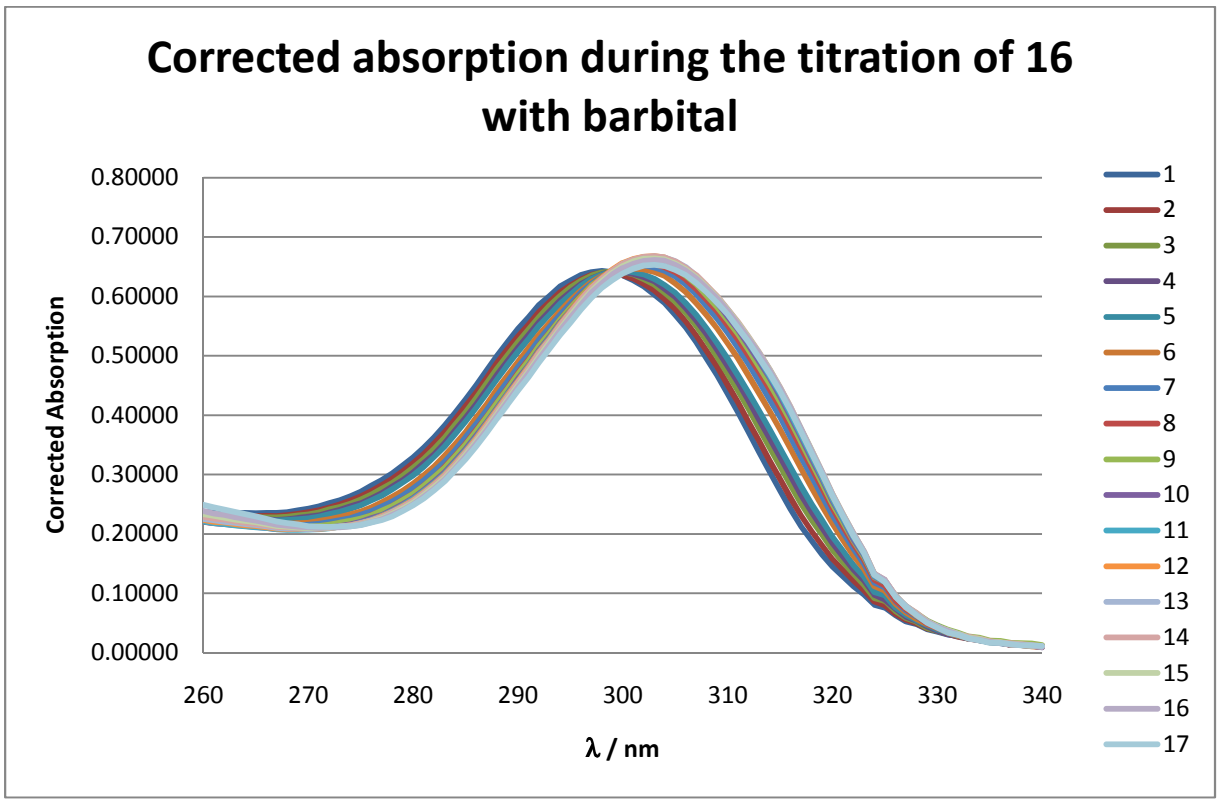

Corrected absorption at 317 nm during the titration of 14 with barbital
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
A corr.(317)
0
5
10
15
20
25
30
35
n

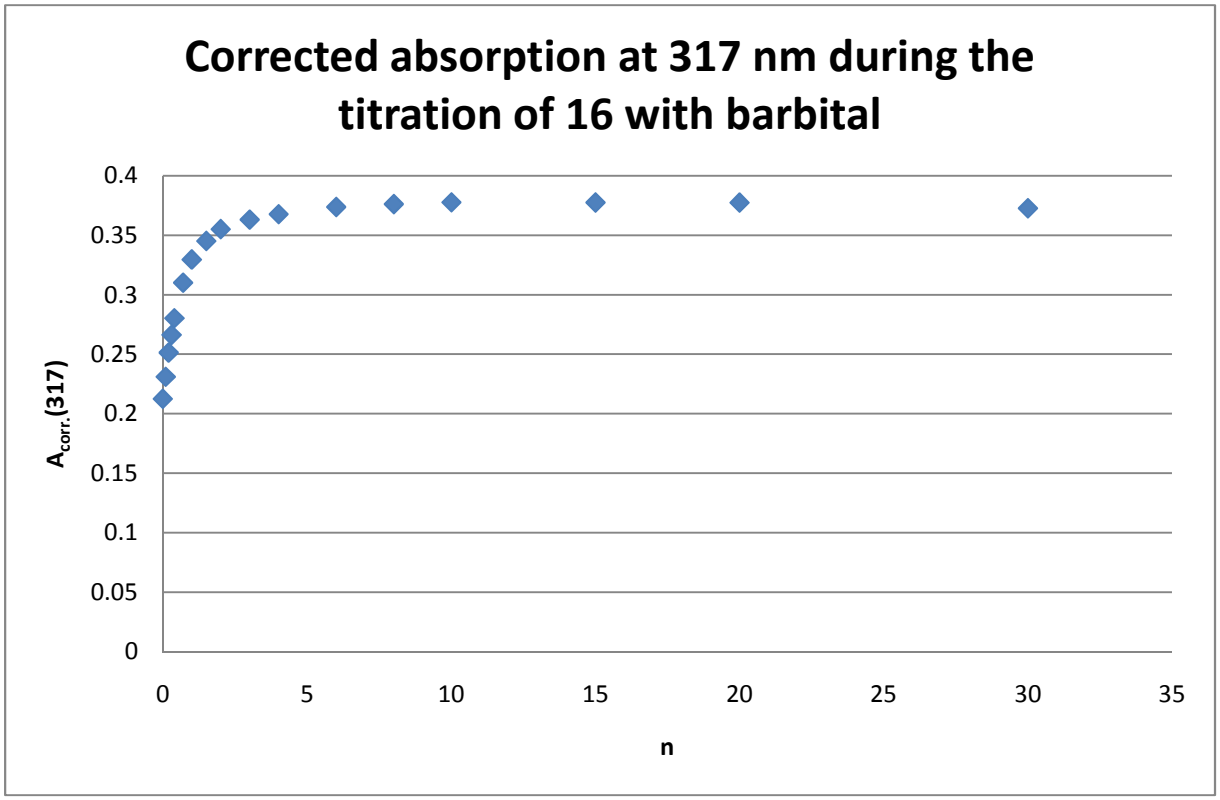

Crude absorption data during the titration of 15 with barbital
3
2.5
2
1.5
1
0.5
0
Absorption
220.0
270.0
320.0
370.0
420.0
470.0
520.0
570.0
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

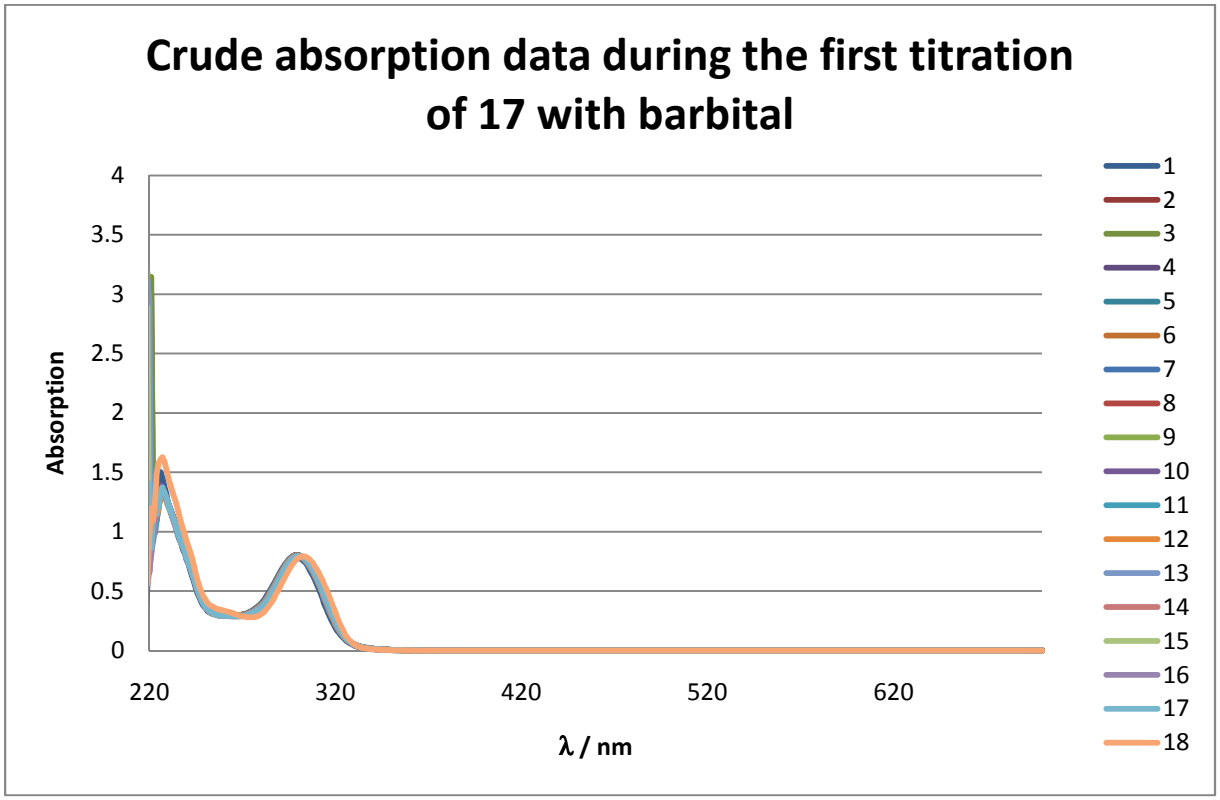

Corrected absorption during the titration of 15 with barbital
Corrected absorption
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
270.0
280.0
290.0
300.0
310.0
320.0
330.0
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

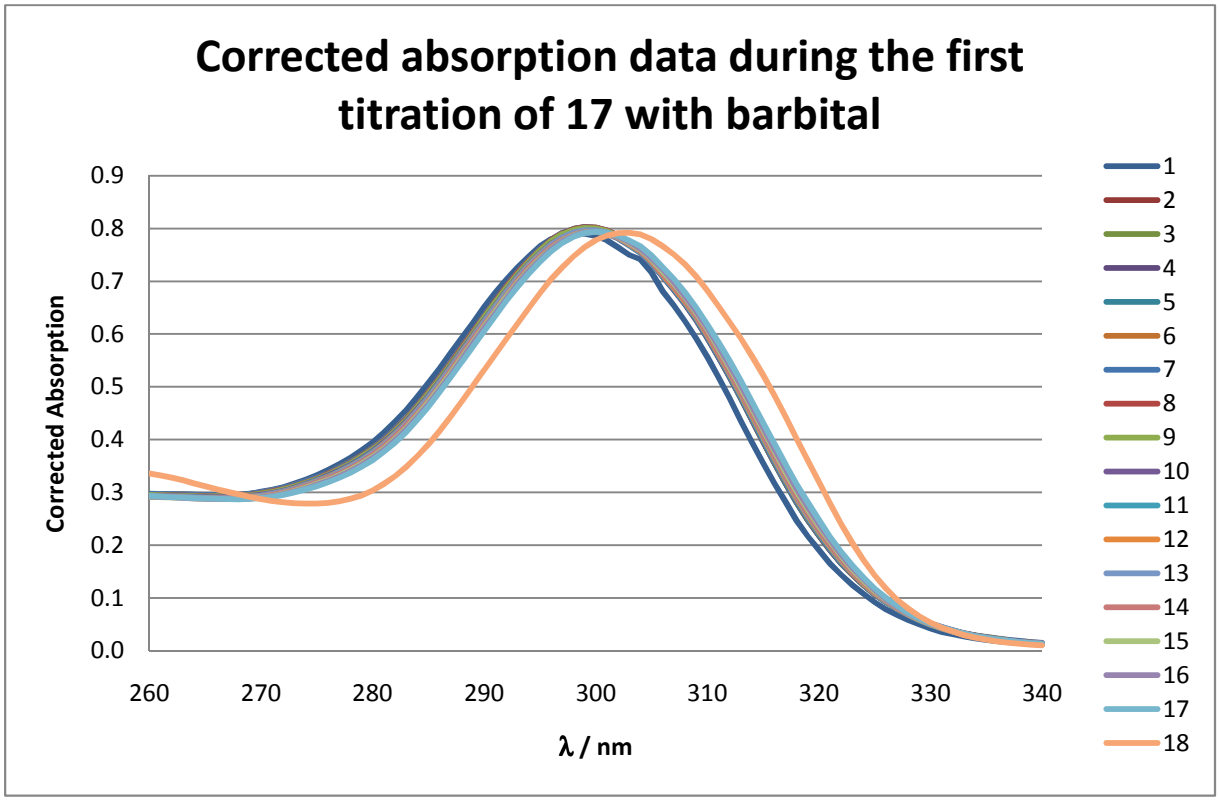

Corrected absorption at 317 nm during the titration of 15 with barbital
A corr.(317)
0.6
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25
30
35
n

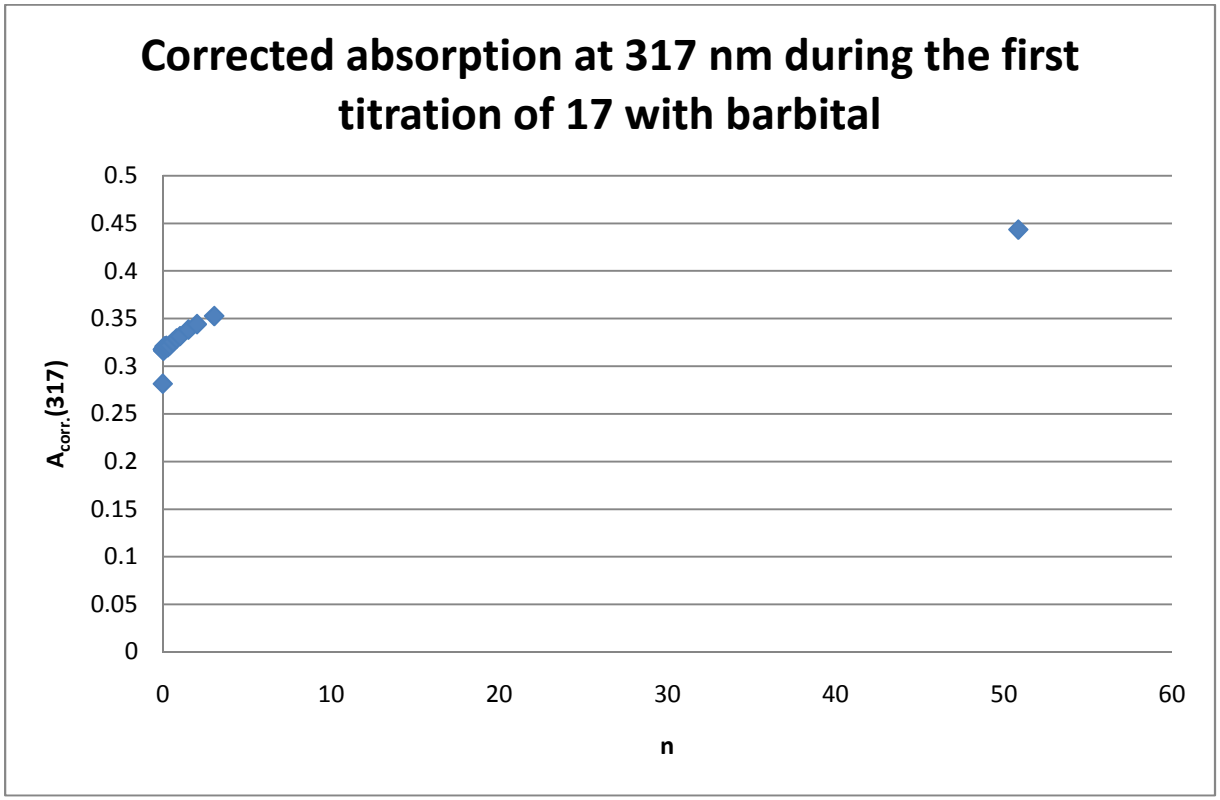

Crude absorption data during the titration of 16 with barbital
Absorption
3
2.5
2
1.5
1
0.5
0
220
320
420
520
620
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

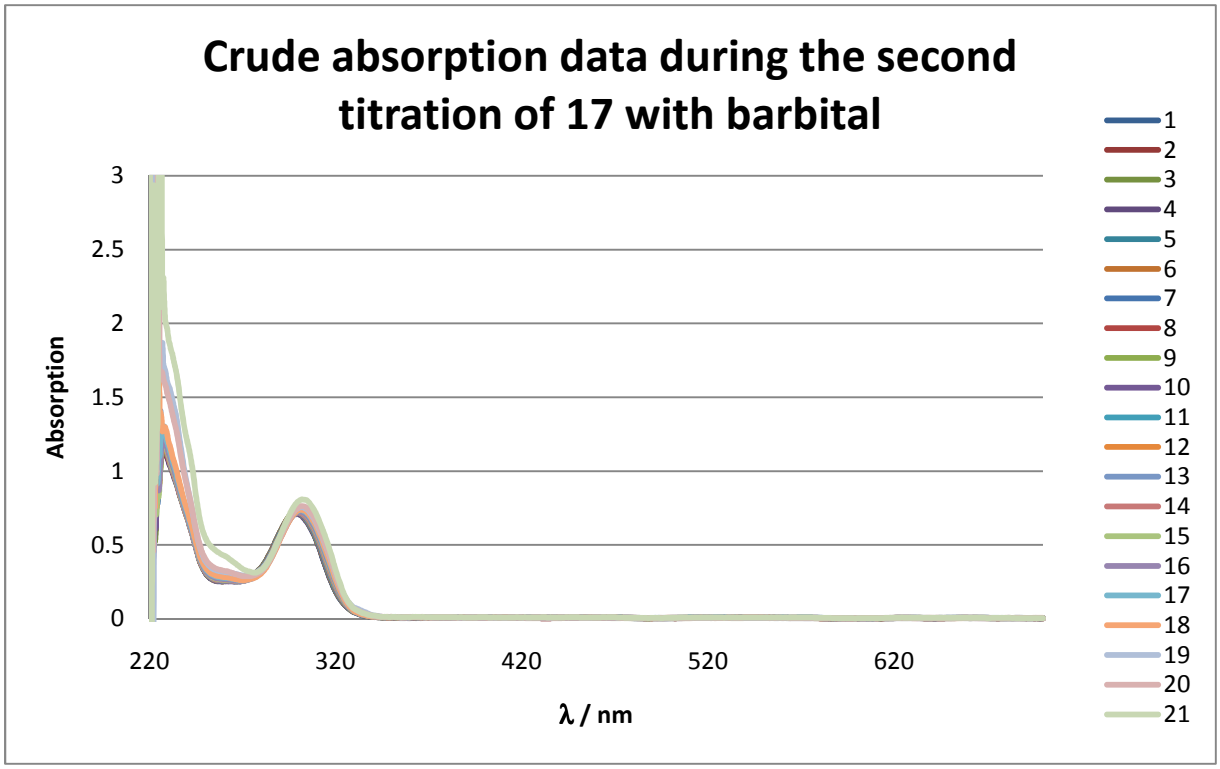

Corrected absorption during the titration of 16 with barbital
Corrected Absorption
0.80000
0.70000
0.60000
0.50000
0.40000
0.30000
0.20000
0.10000
0.00000
260
270
280
290
300
310
320
330
340
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

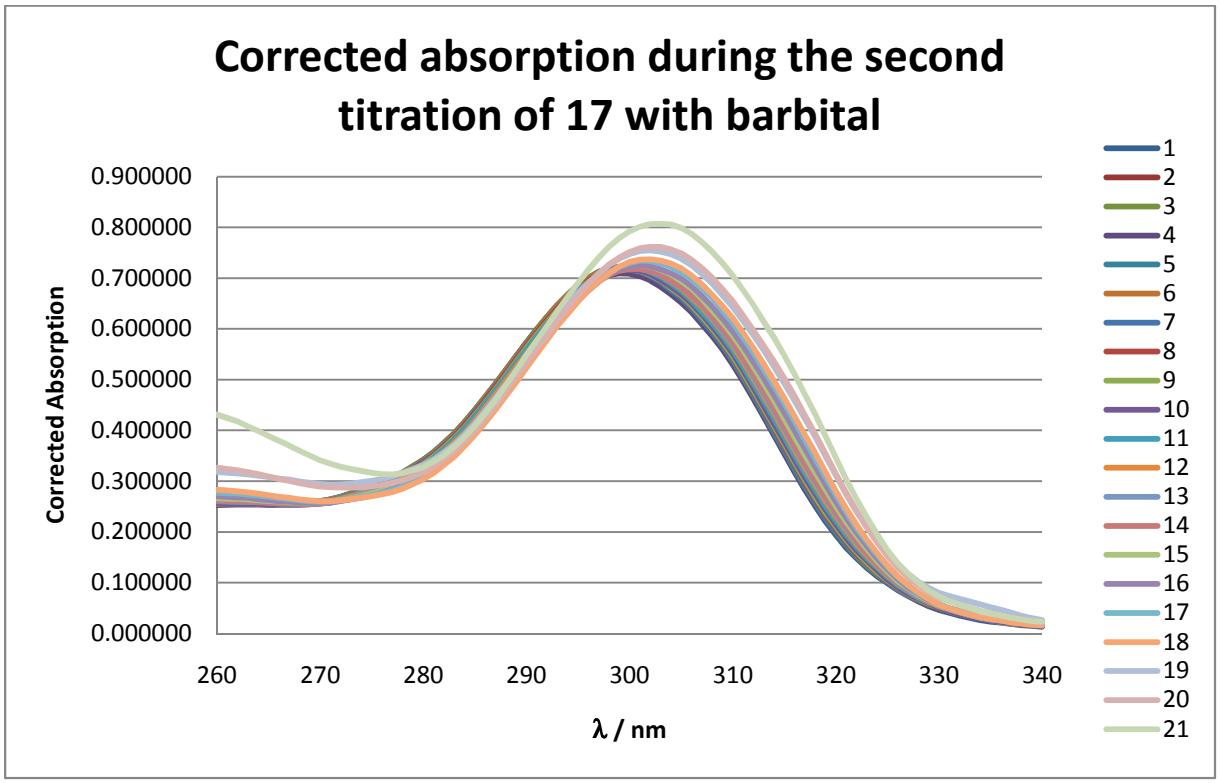

Corrected absorption at 317 nm during the titration of 16 with barbital
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
A corr.(317)
0
5
10
15
20
25
30
35
n

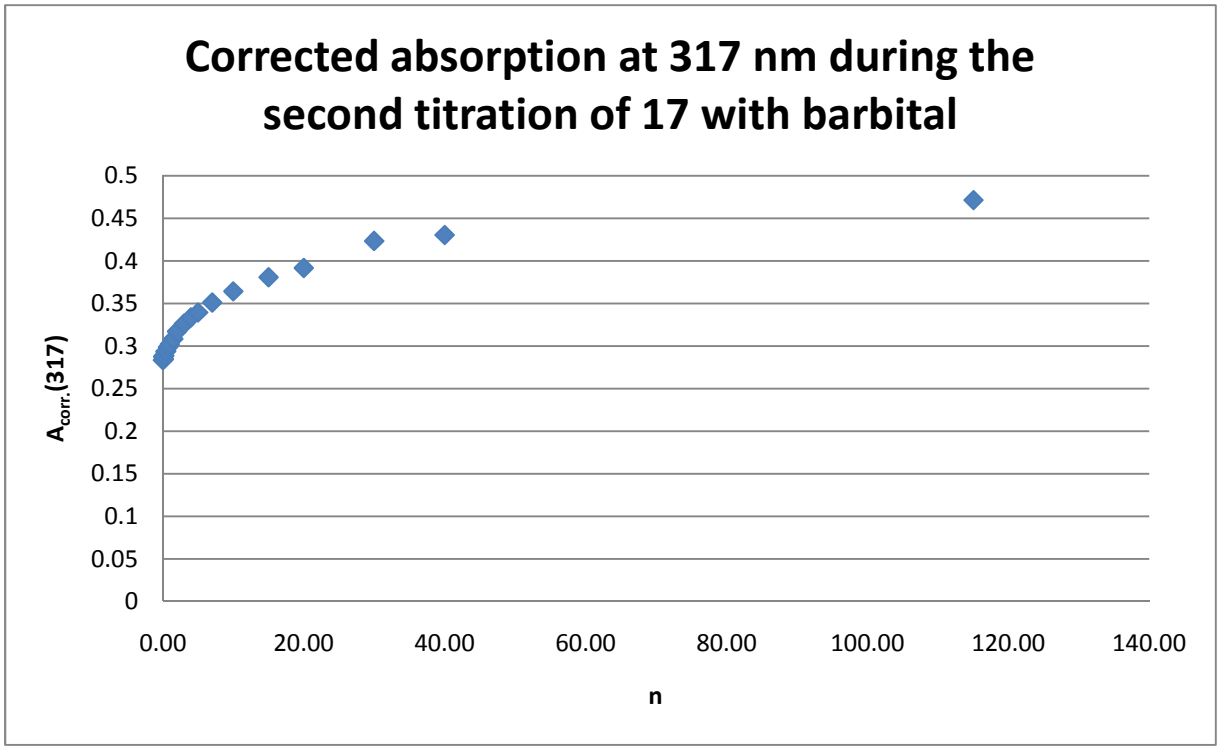

Crude absorption data during the first titration of 17 with barbital
4
3.5
3
2.5
2
1.5
1
0.5
0
Absorption
220
320
420
520
620
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

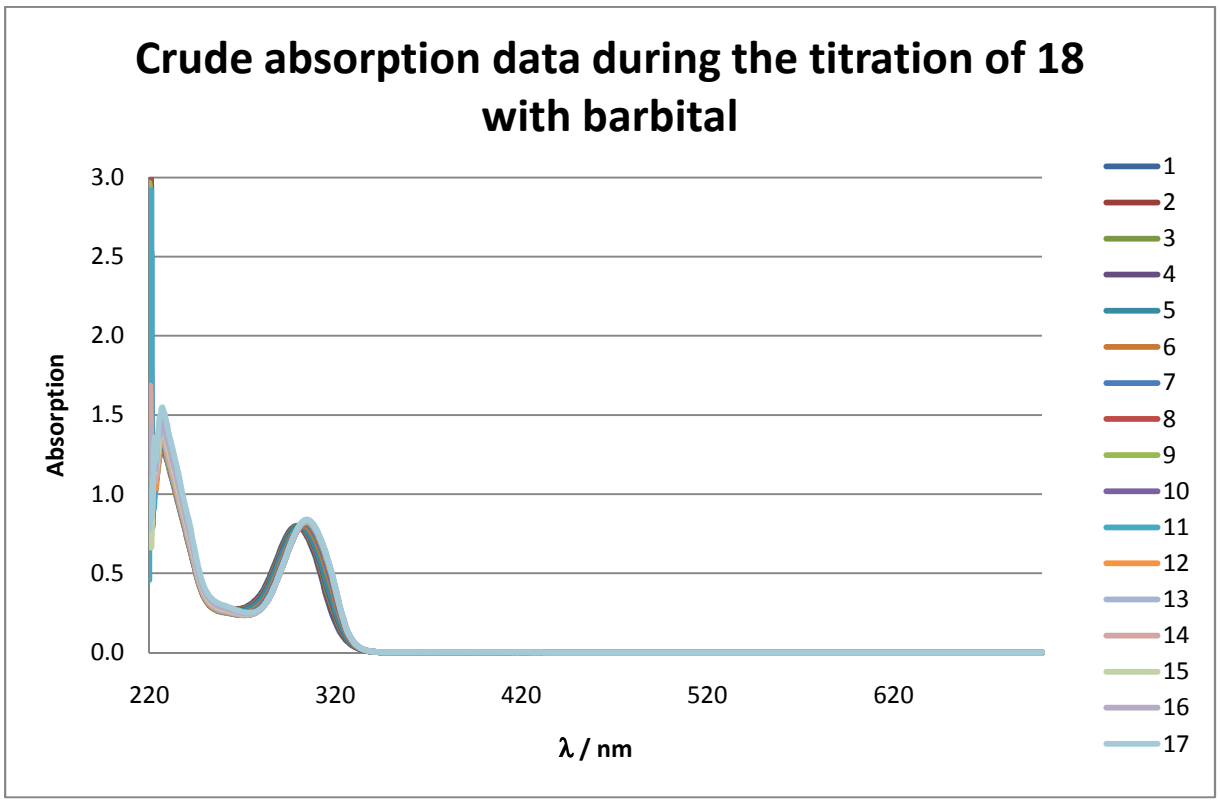

Corrected absorption data during the first titration of 17 with barbital
Corrected Absorption
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
260
270
280
290
300
310
320
330
340
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

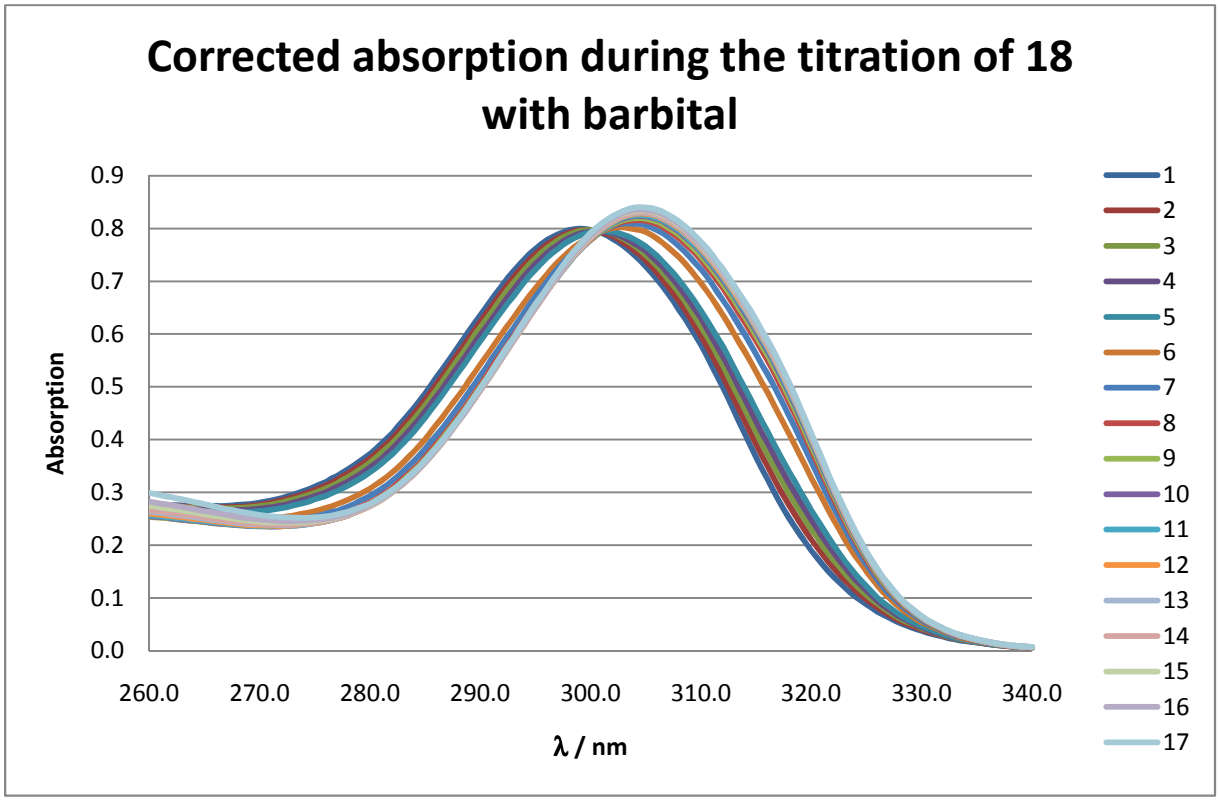

Corrected absorption at 317 nm during the first titration of 17 with barbital
A corr.(317)
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
10
20
30
40
50
60
n

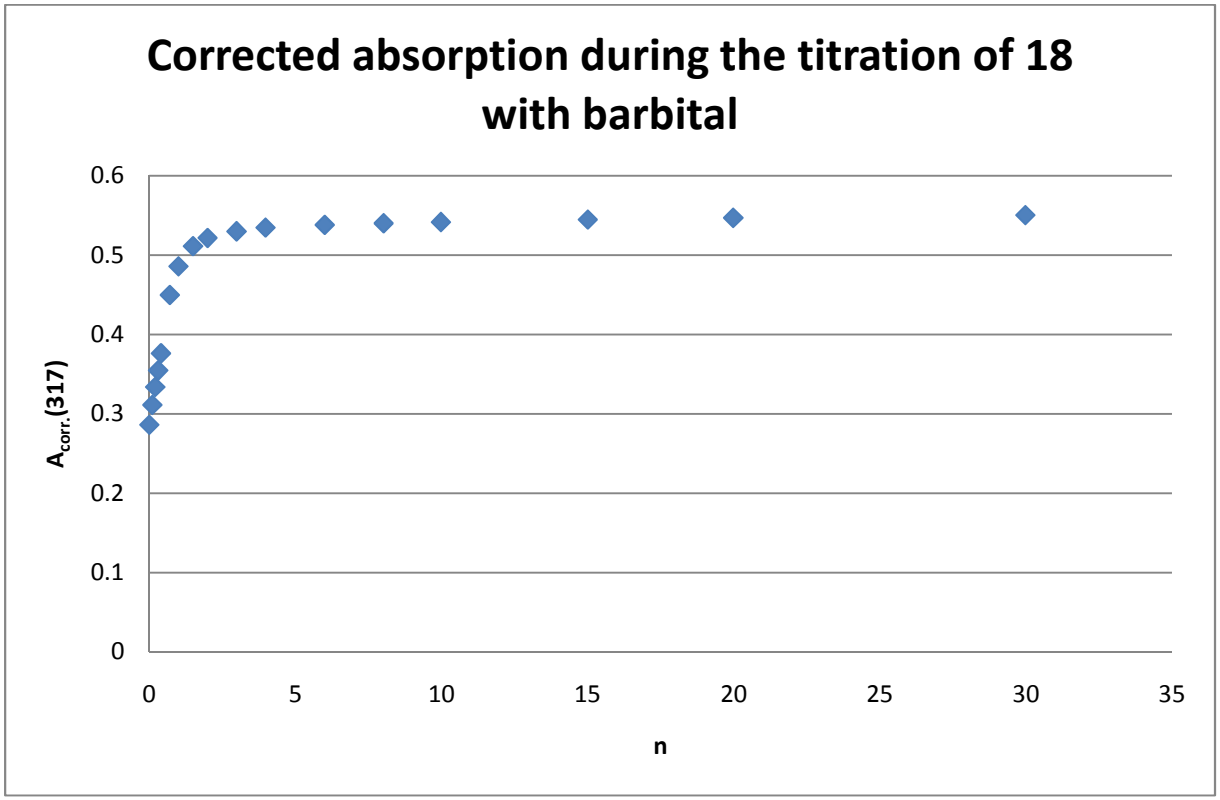

Crude absorption data during the second titration of 17 with barbital
Absorption
3
2.5
2
1.5
1
0.5
0
220
320
420
520
620
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21

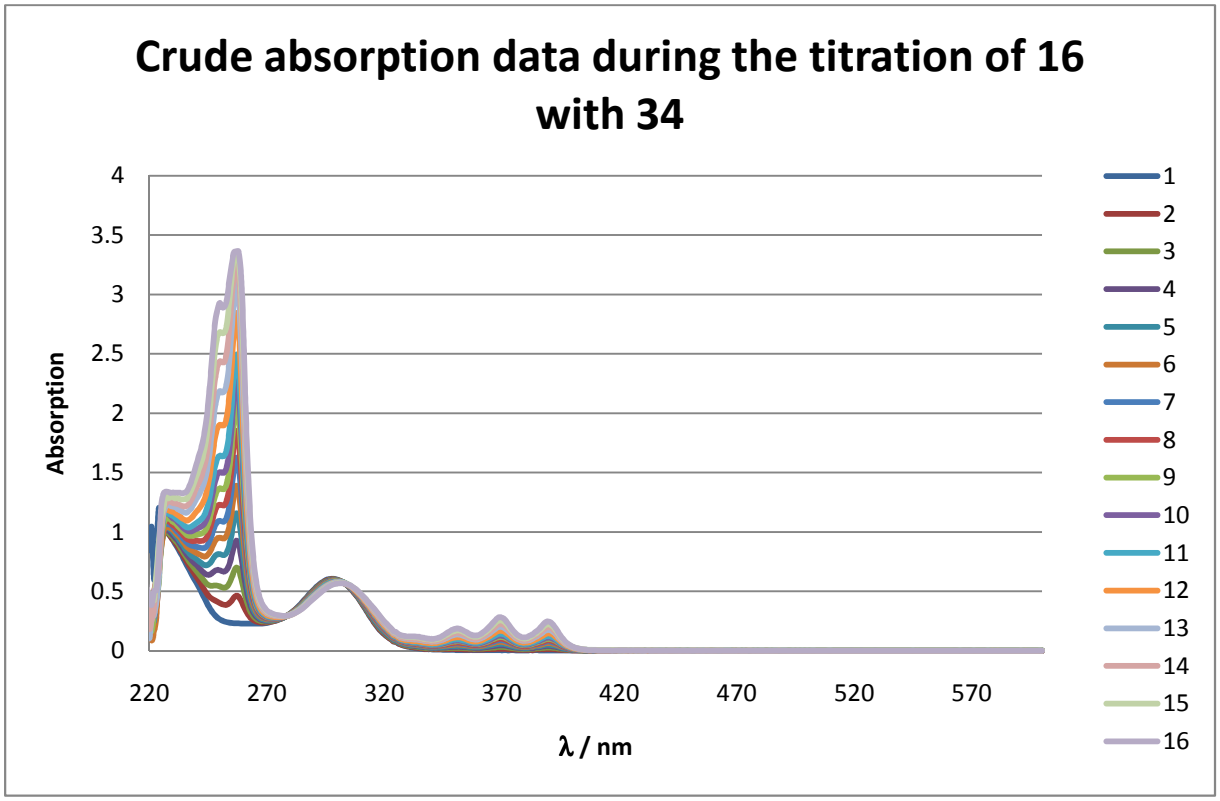

Corrected absorption during the second titration of 17 with barbital
Corrected Absorption
0.900000
0.800000
0.700000
0.600000
0.500000
0.400000
0.300000
0.200000
0.100000
0.000000
260
270
280
290
300
310
320
330
340
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21

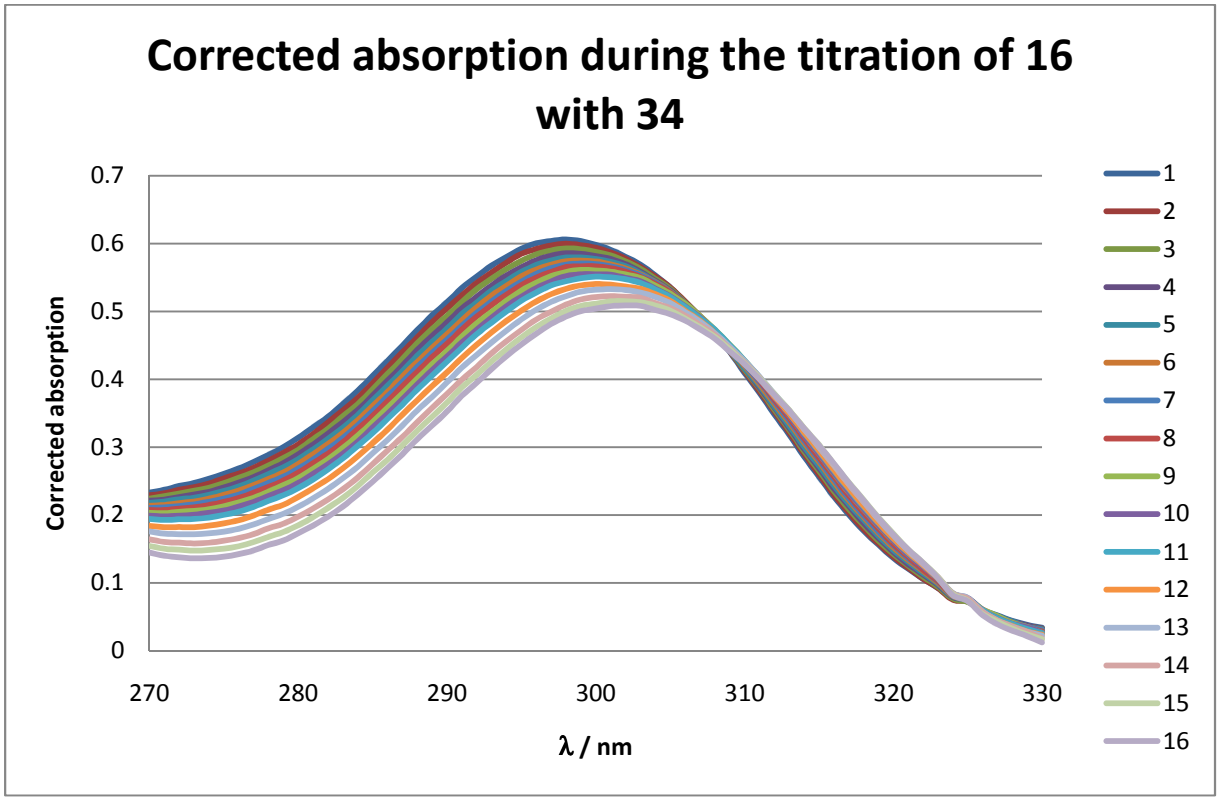

Corrected absorption at 317 nm during the second titration of 17 with barbital
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
A corr.(317)
0.00
20.00
40.00
60.00
80.00
100.00
120.00
140.00
n

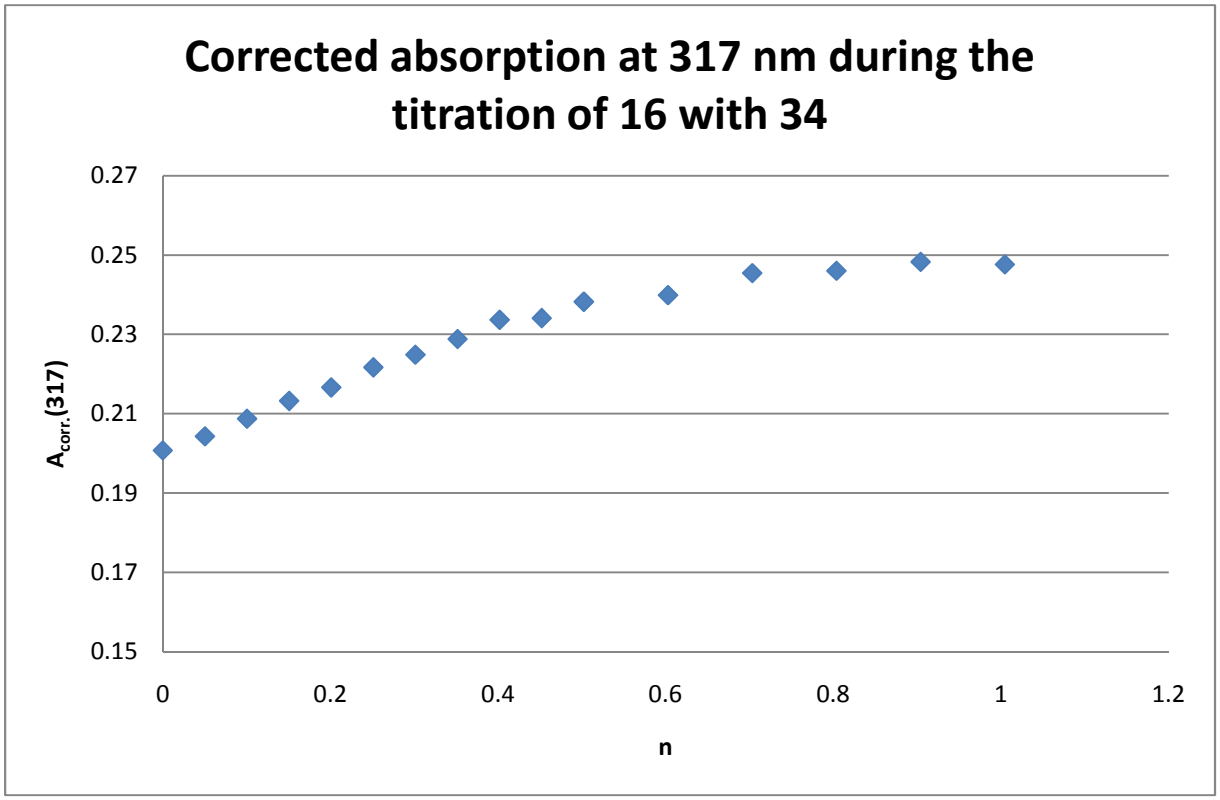

Crude absorption data during the titration of 18 with barbital
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Absorption
220
320
420
520
620
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

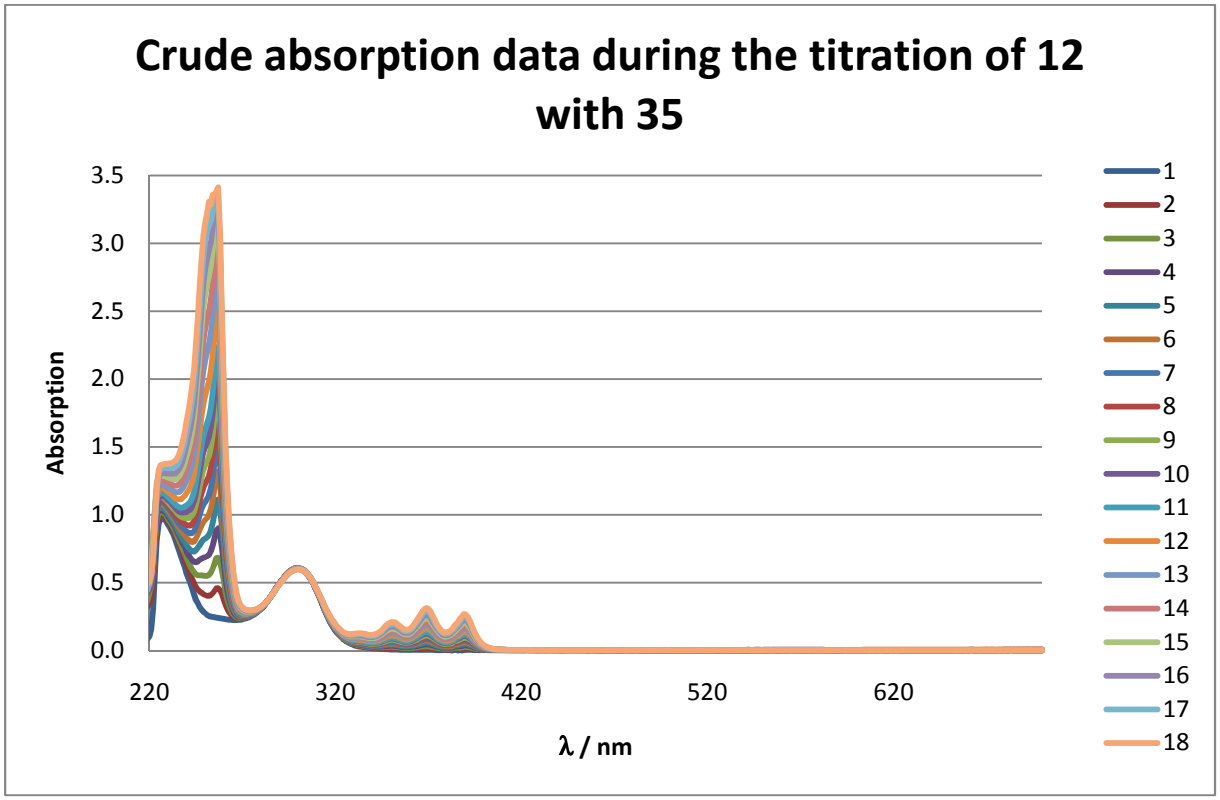

Corrected absorption during the titration of 18 with barbital
Absorption
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
260.0
270.0
280.0
290.0
300.0
310.0
320.0
330.0
340.0
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

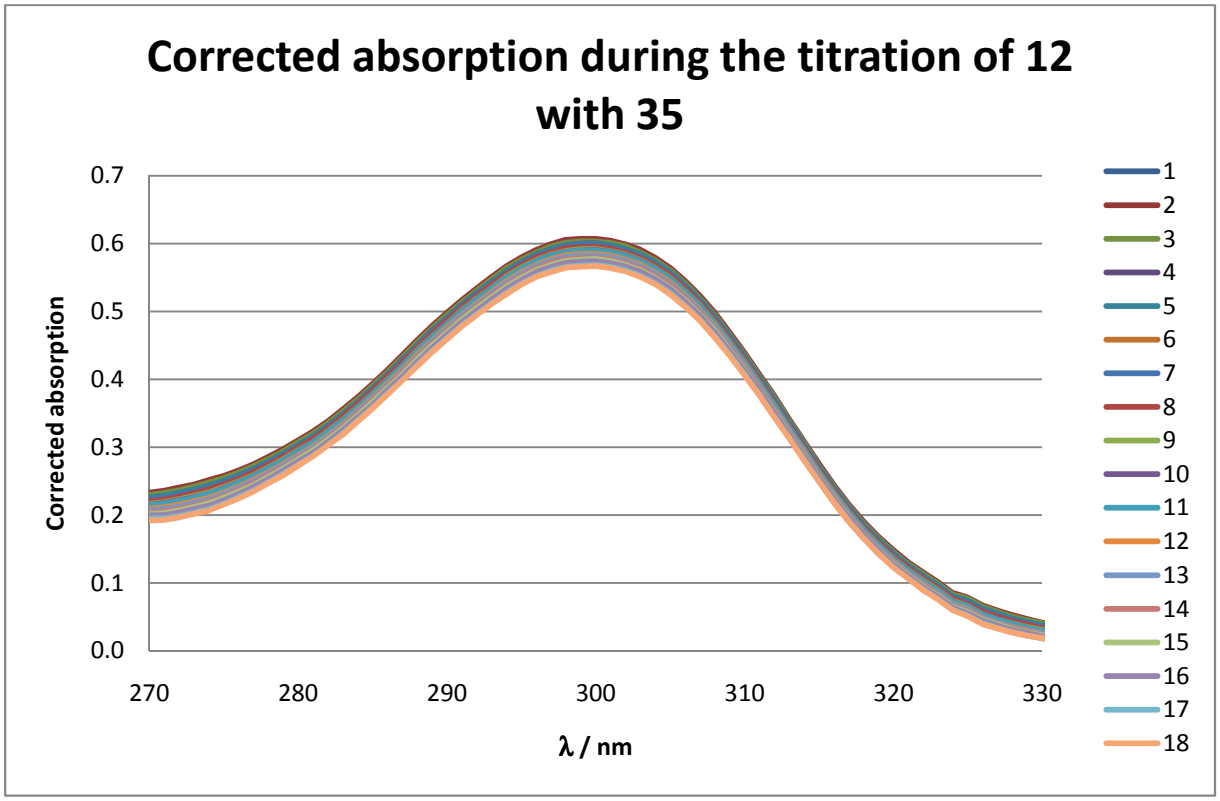

Corrected absorption during the titration of 18 with barbital
A corr.(317)
0.6
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25
30
35
n

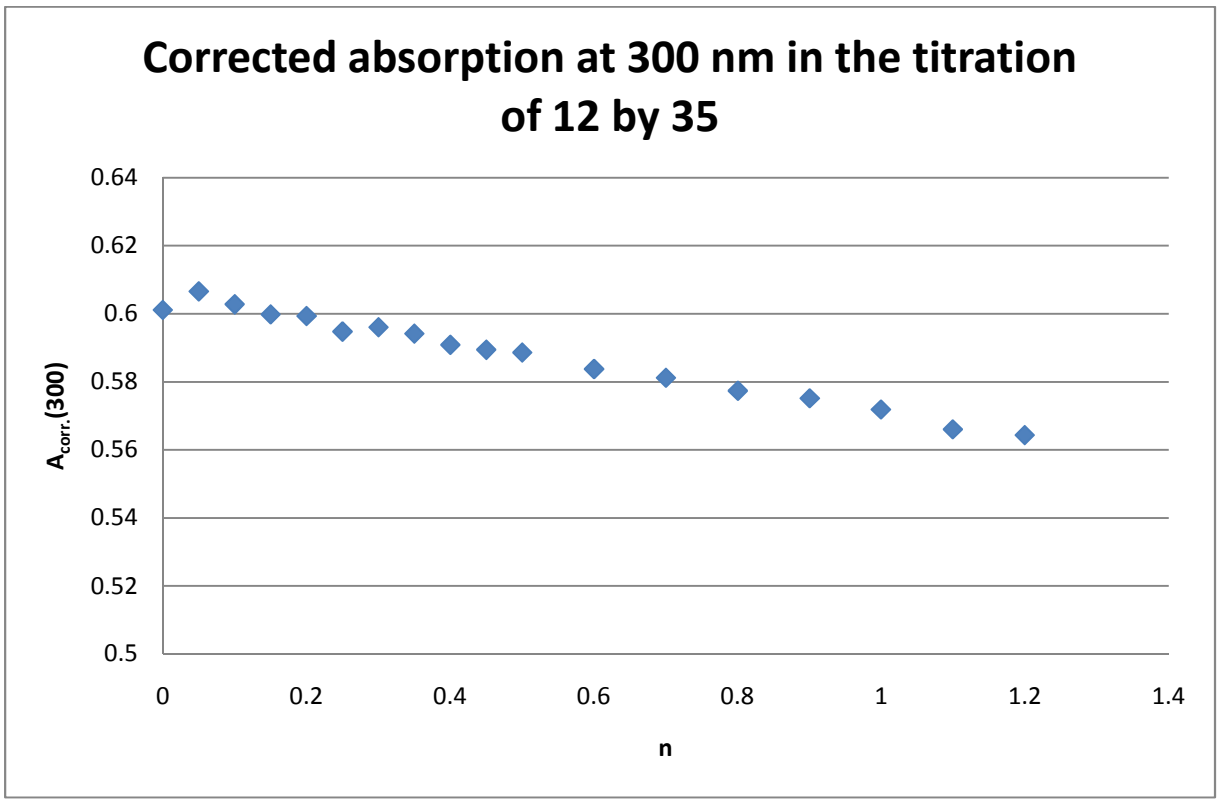

Crude absorption data during the titration of 16 with 34
Absorption
λ / nm
4
3.5
3
2.5
2
1.5
1
0.5
0
220
270
320
370
420
470
520
570
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

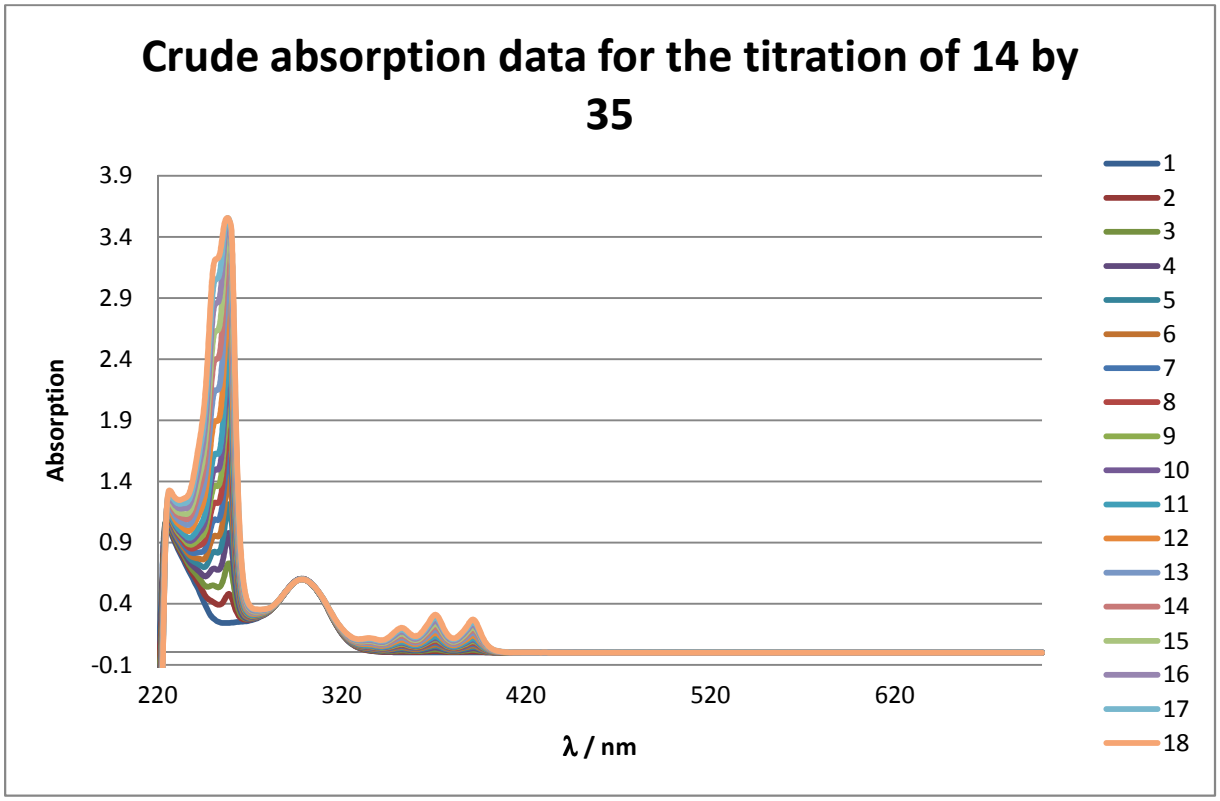

Corrected absorption during the titration of 16 with 34
Corrected absorption
λ / nm
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
270
280
290
300
310
320
330
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

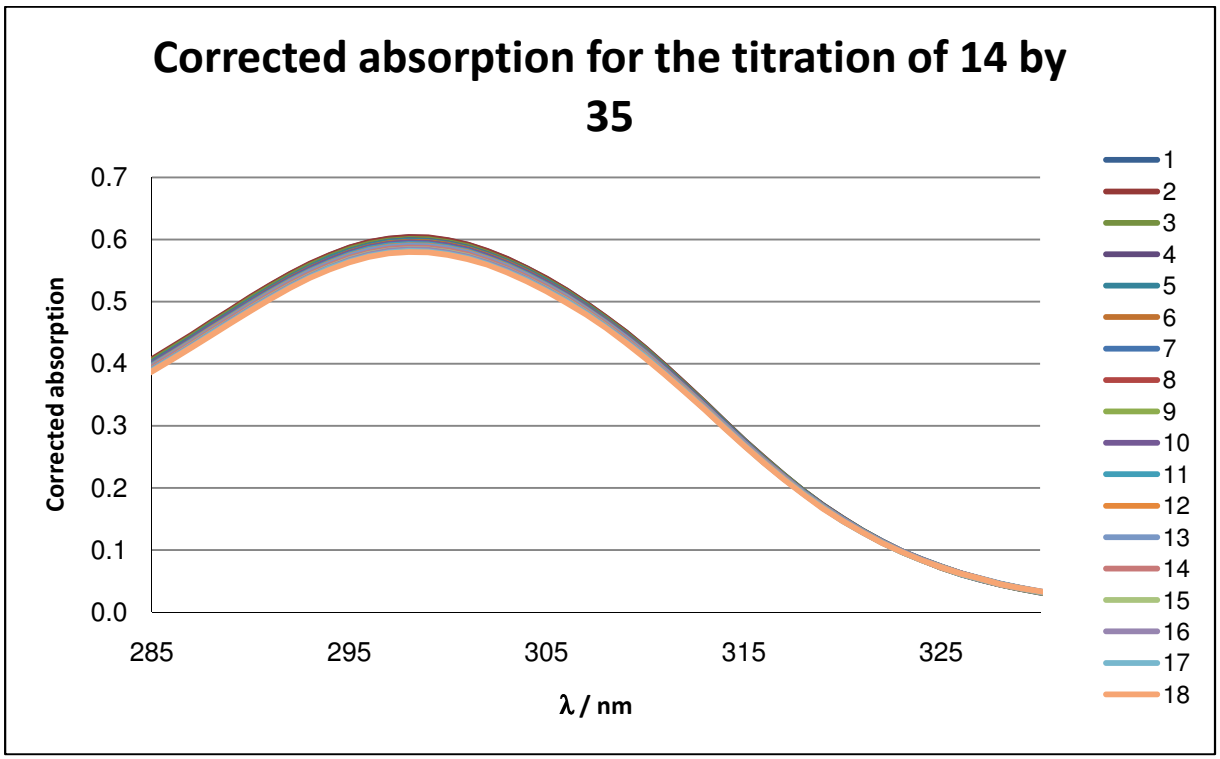

Corrected absorption at 317 nm during the titration of 16 with 34
0.27
0.25
0.23
0.21
0.19
0.17
0.15
A corr.(317)
0
0.2
0.4
0.6
0.8
1
1.2
n

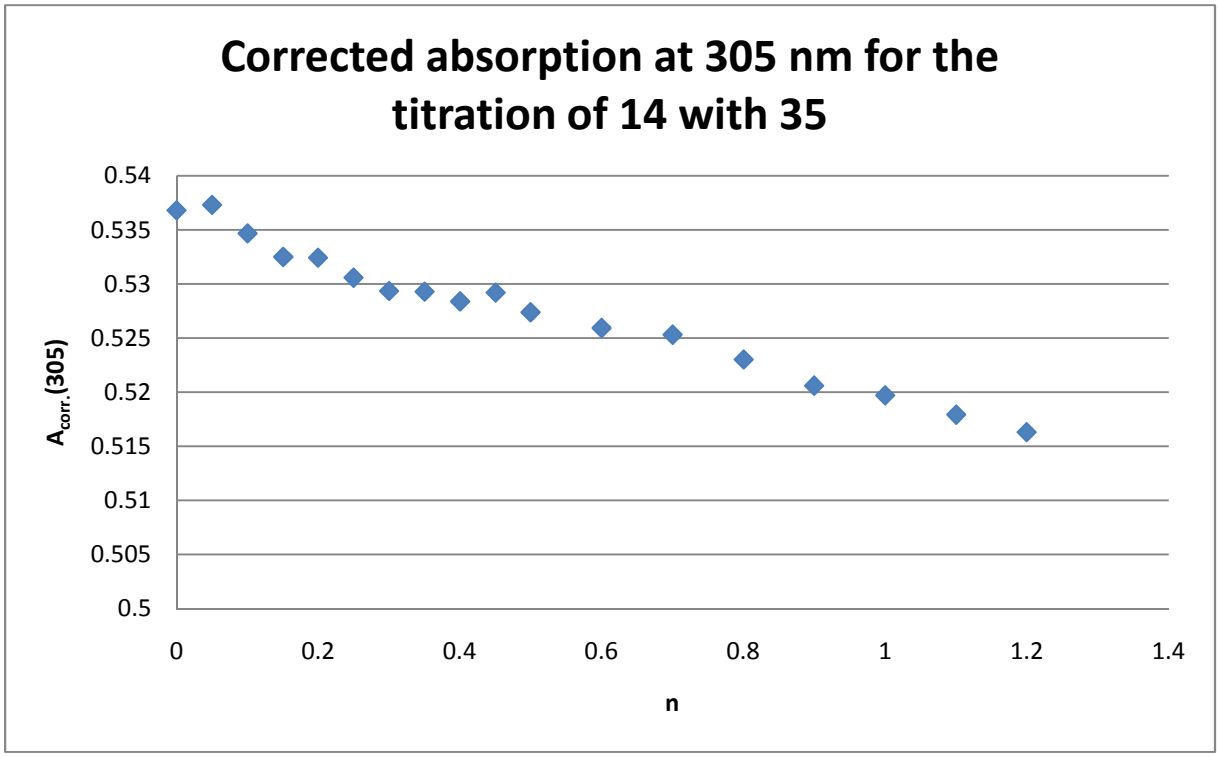

Crude absorption data during the titration of 12 with 35
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Absorption
220
320
420
520
620
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

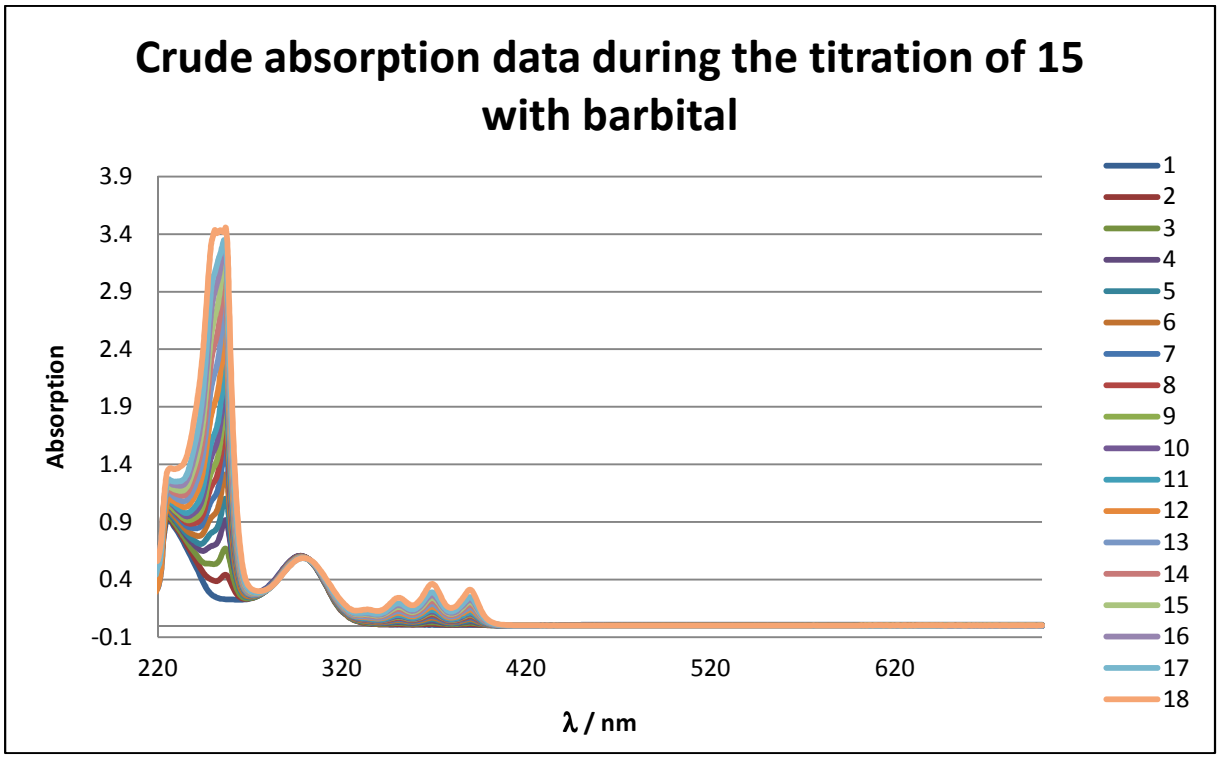

Corrected absorption during the titration of 12 with 35
Corrected absorption
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
270
280
290
300
310
320
330
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

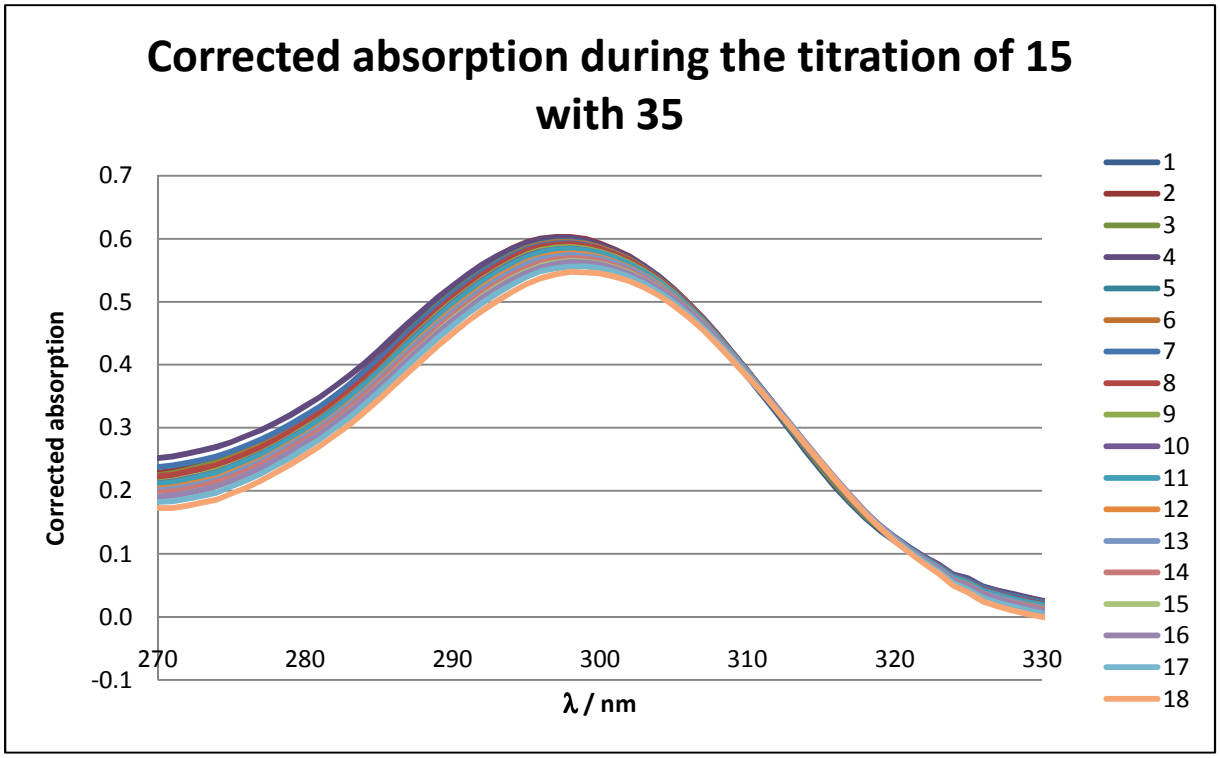

Corrected absorption at 300 nm in the titration of 12 by 35
$A_{corr.}(300)$
0.64
0.62
0.6
0.58
0.56
0.54
0.52
0.5
0
0.2
0.4
0.6
0.8
1
1.2
1.4
n

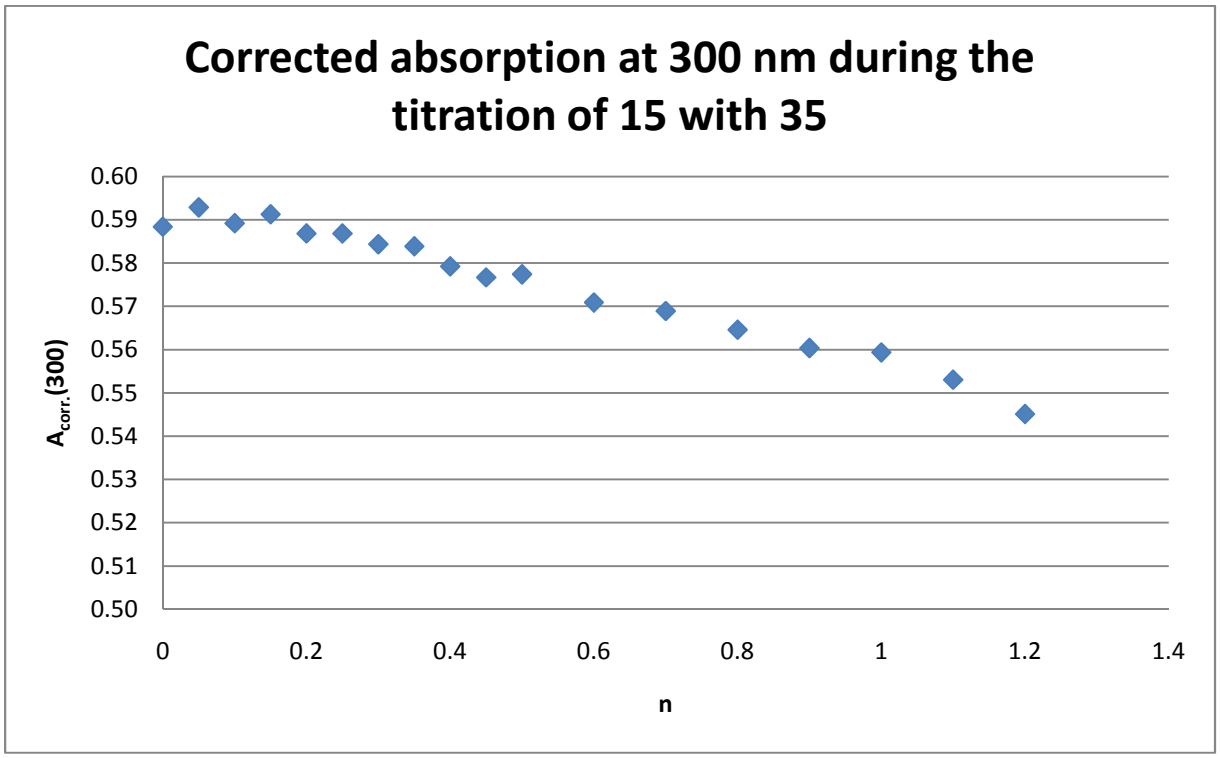

Crude absorption data for the titration of 14 by 35
Absorption
3.9
3.4
2.9
2.4
1.9
1.4
0.9
0.4
-0.1
220
320
420
520
620
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

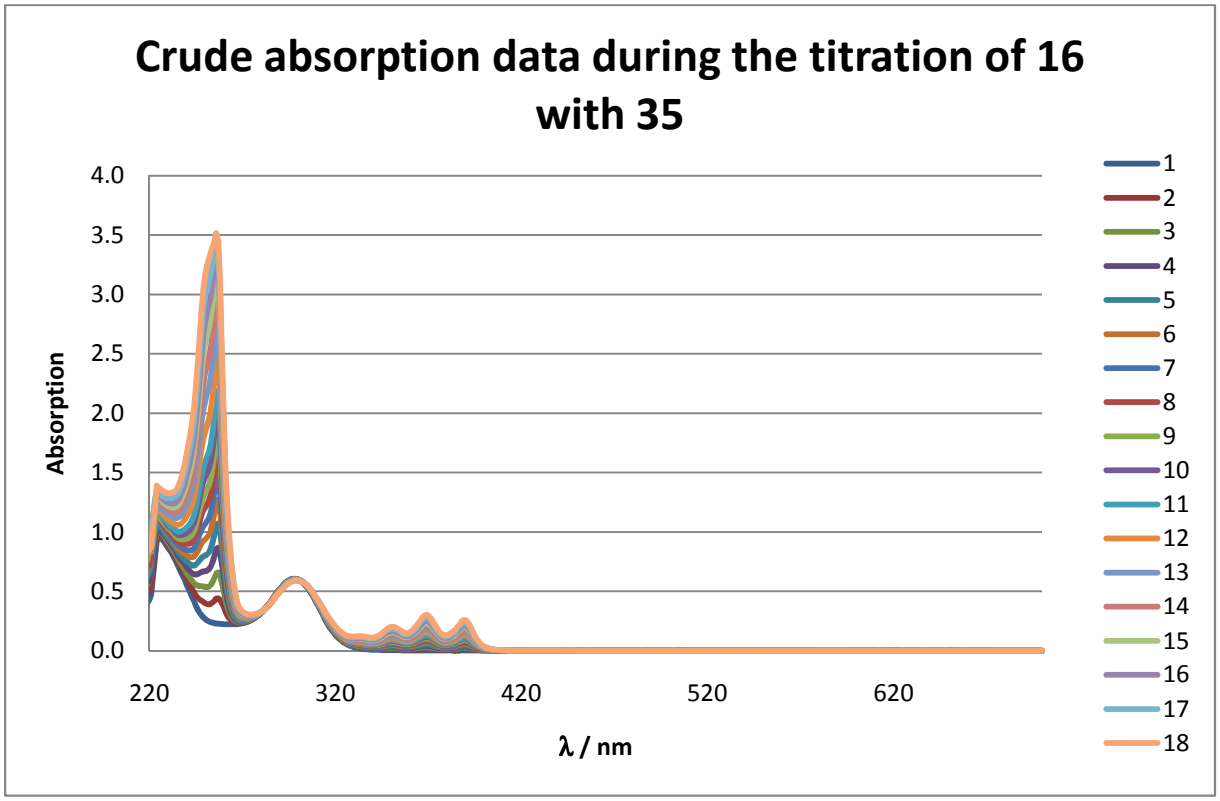

Corrected absorption for the titration of 14 by 35
Corrected absorption
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
285
295
305
315
325
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

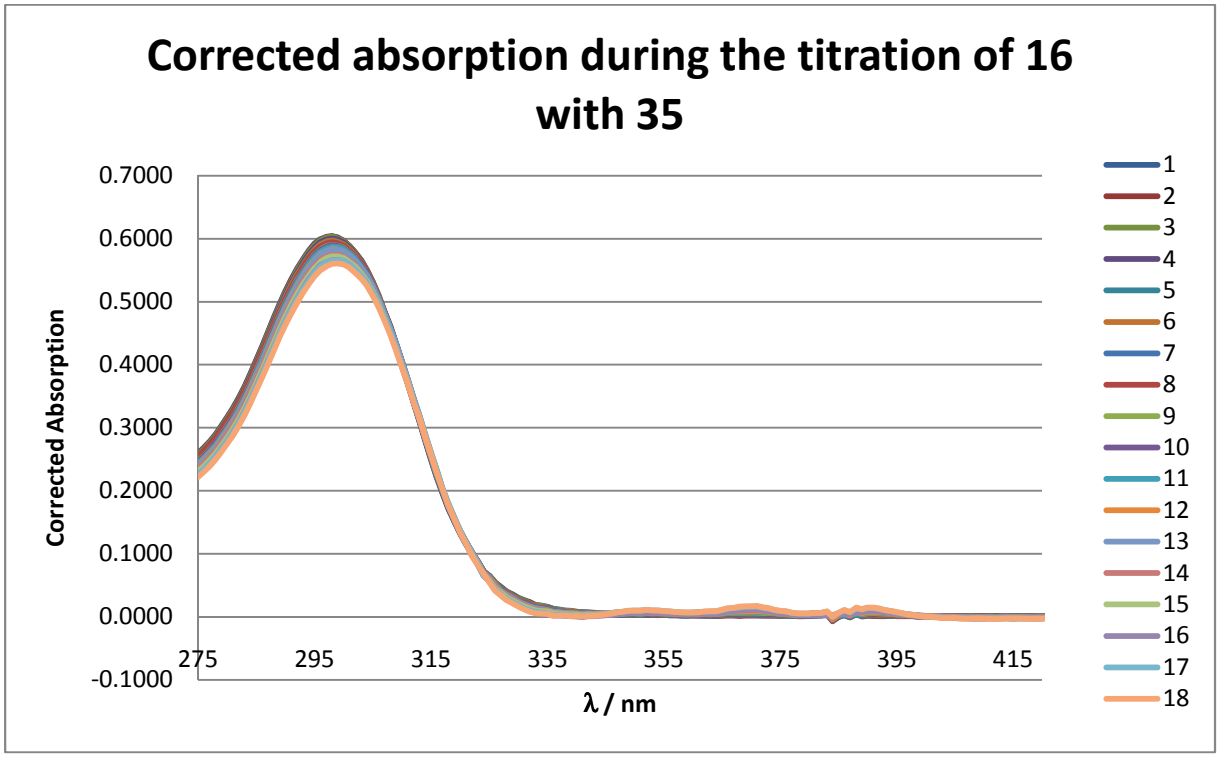

Corrected absorption at 305 nm for the titration of 14 with 35
0.54
0.535
0.53
0.525
0.52
0.515
0.51
0.505
0.5
A corr.(305)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
n

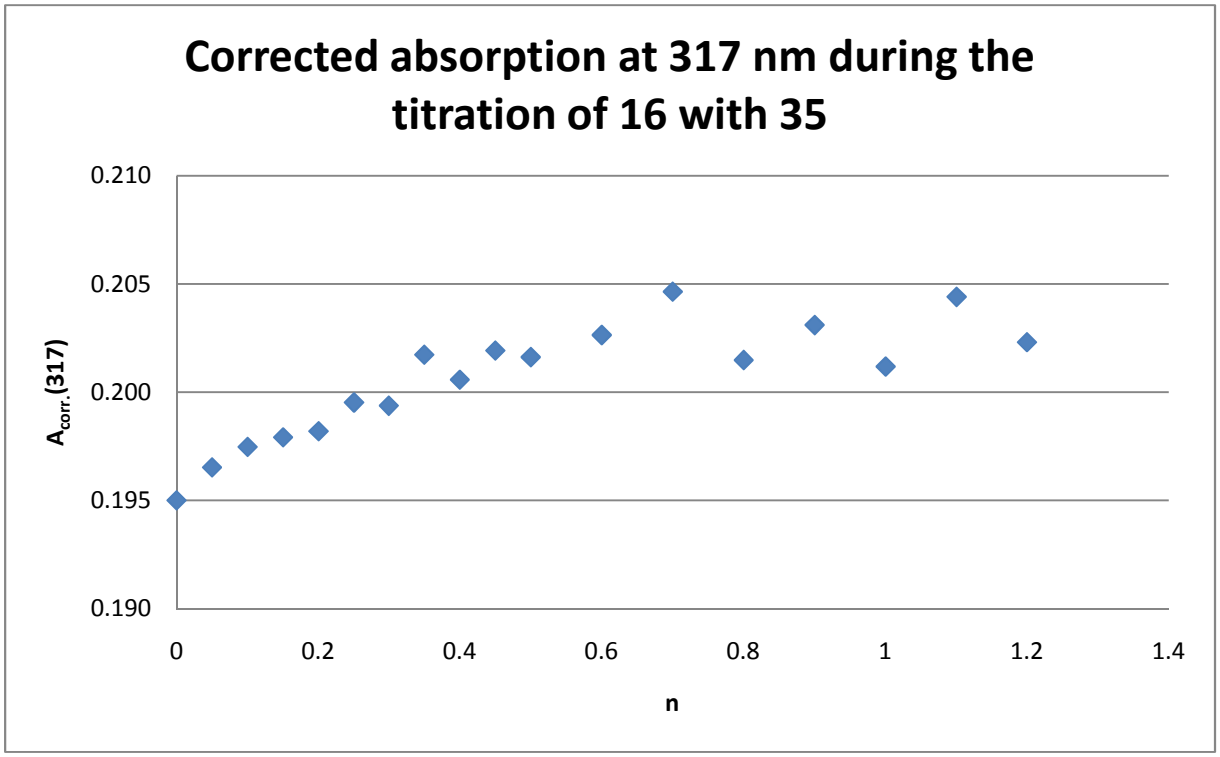

Crude absorption data during the titration of 15 with barbital
3.9
3.4
2.9
2.4
1.9
1.4
0.9
0.4
-0.1
Absorption
220
320
420
520
620
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

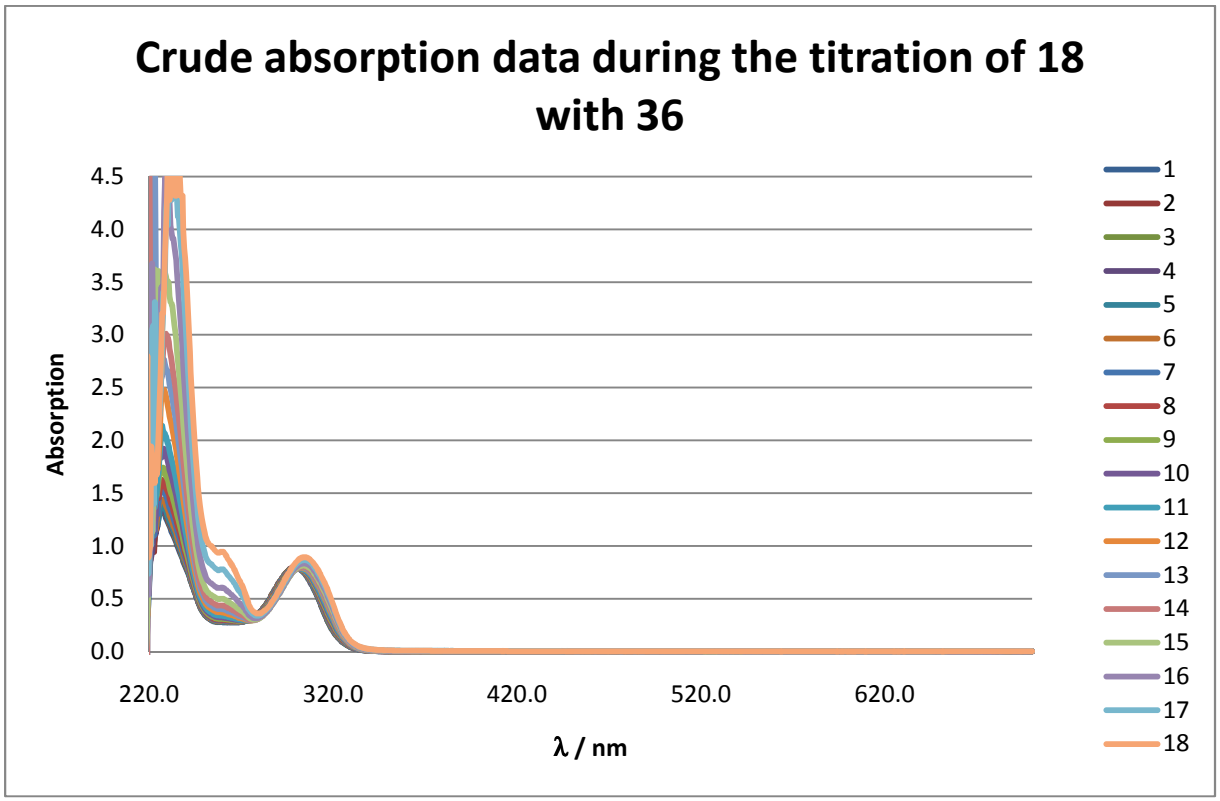

Corrected absorption during the titration of 15 with 35
Corrected absorption
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
270
280
290
300
310
320
330
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

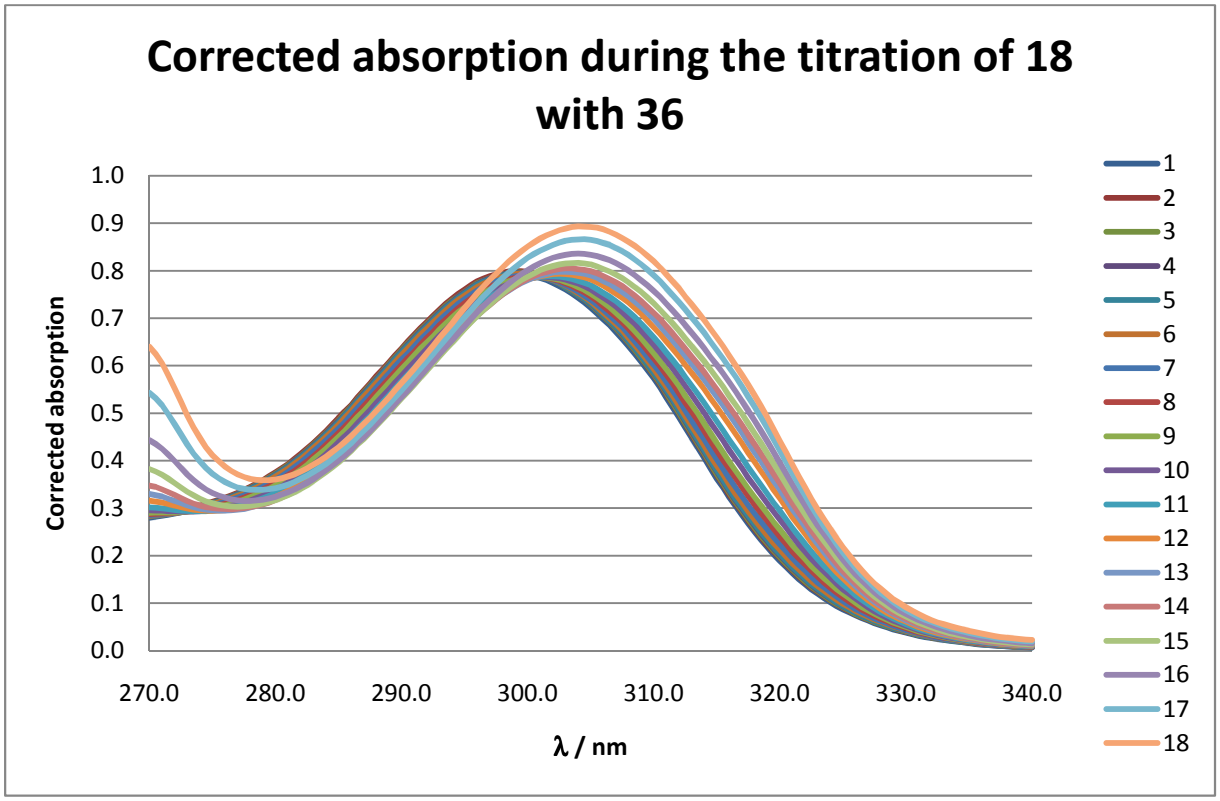

Corrected absorption at 300 nm during the titration of 15 with 35
$A_{corr.}(300)$
0.60
0.59
0.58
0.57
0.56
0.55
0.54
0.53
0.52
0.51
0.50
0
0.2
0.4
0.6
0.8
1
1.2
1.4
n

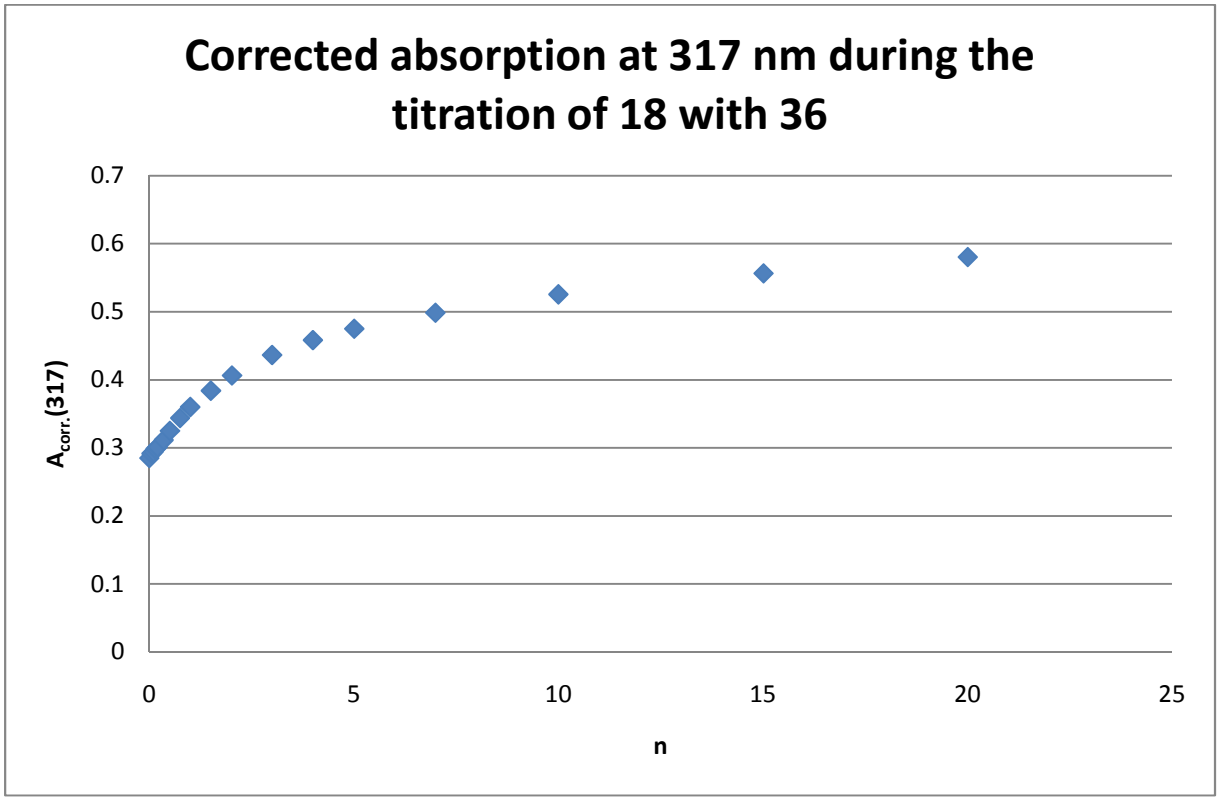

Crude absorption data during the titration of 16 with 35
Absorption
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
220
320
420
520
620
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

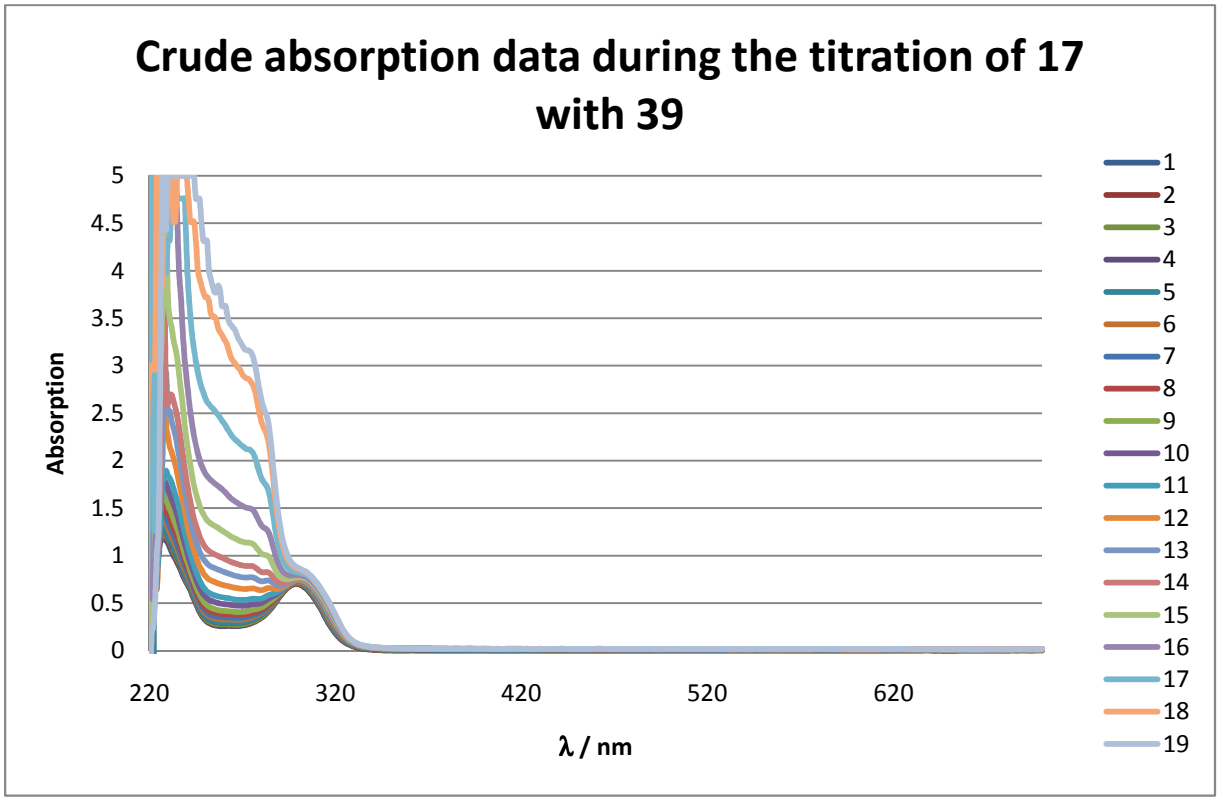

Corrected absorption during the titration of 16 with 35
Corrected Absorption
0.7000
0.6000
0.5000
0.4000
0.3000
0.2000
0.1000
0.0000
-0.1000
275
295
315
335
355
375
395
415
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

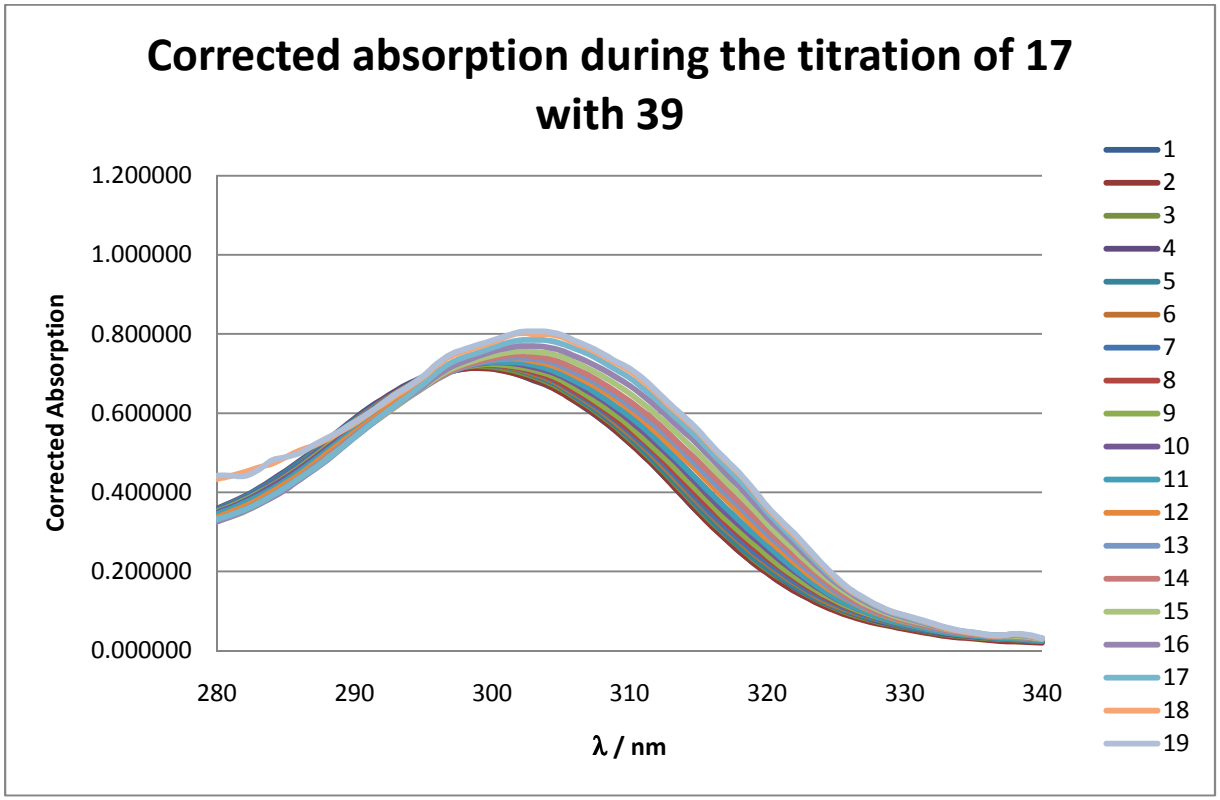

Corrected absorption at 317 nm during the titration of 16 with 35
0.210
0.205
0.200
0.195
0.190
A corr.(317)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
n

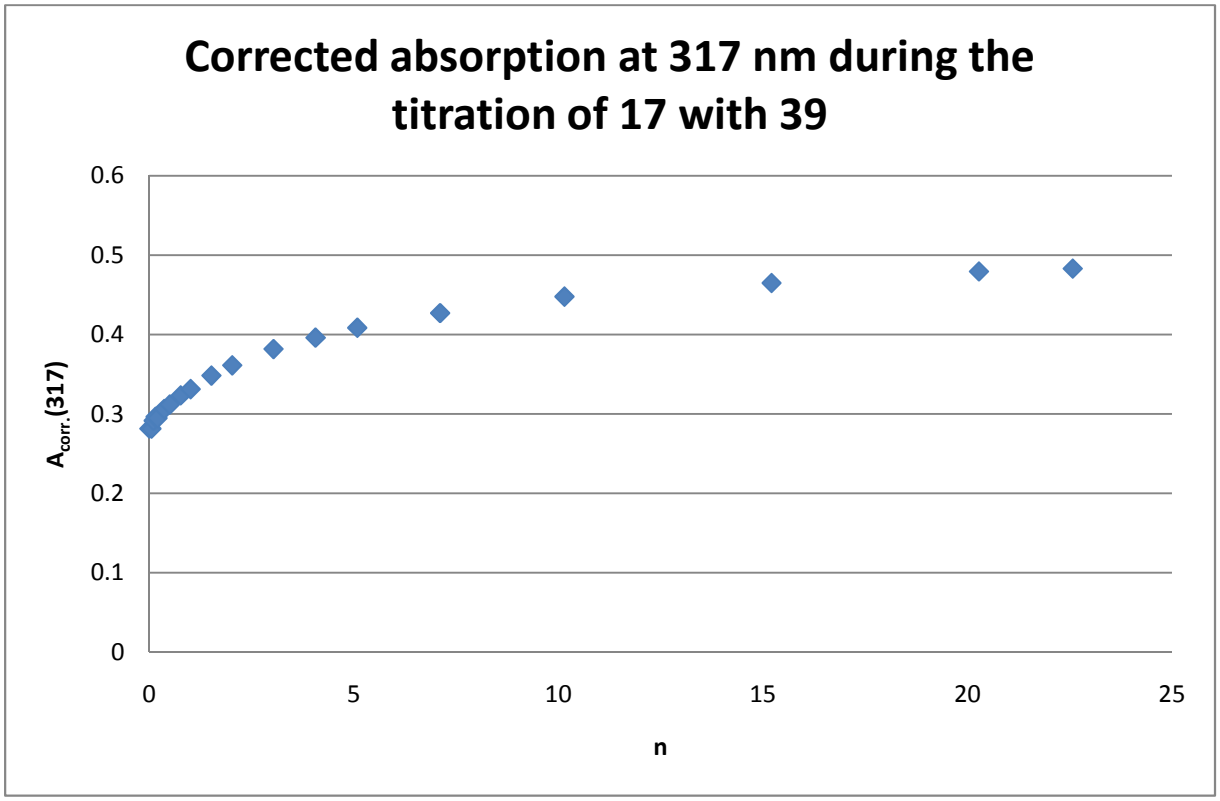

Crude absorption data during the titration of 18 with 36
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Absorption
220.0
320.0
420.0
520.0
620.0
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

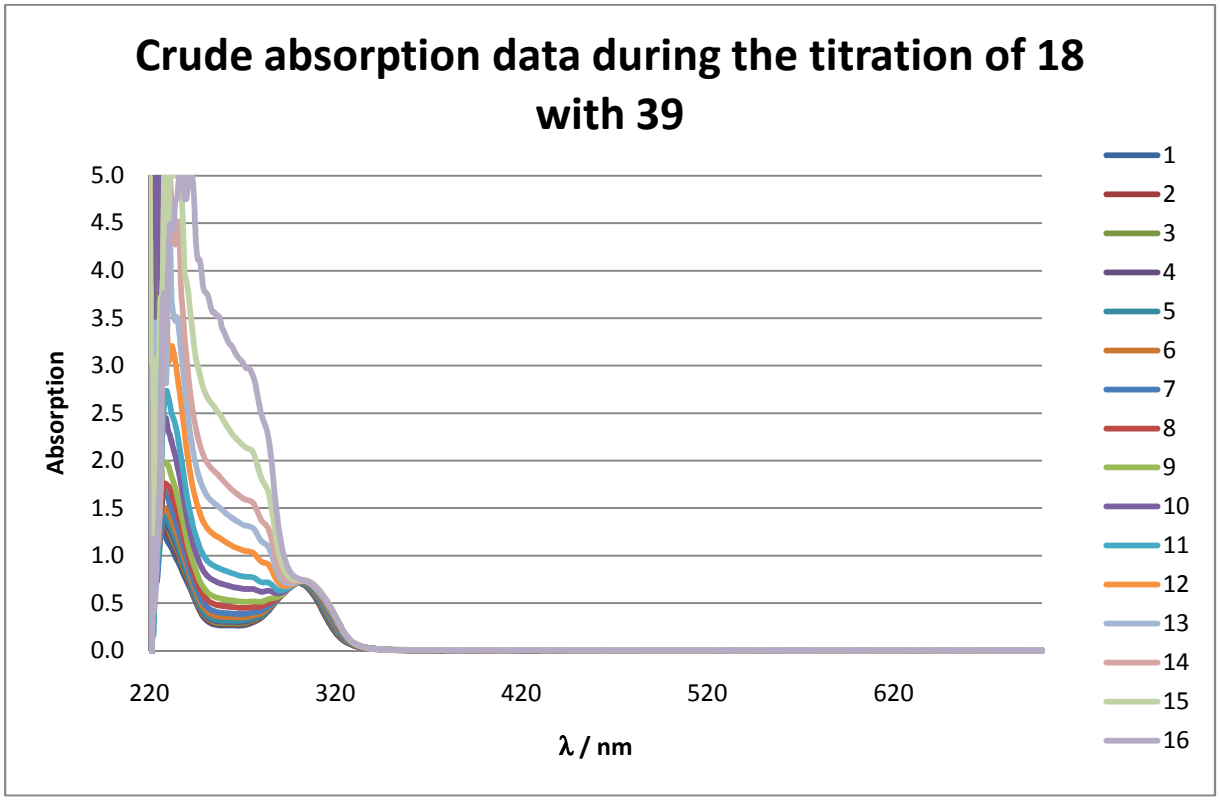

Corrected absorption during the titration of 18 with 36
Corrected absorption
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
270.0
280.0
290.0
300.0
310.0
320.0
330.0
340.0
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

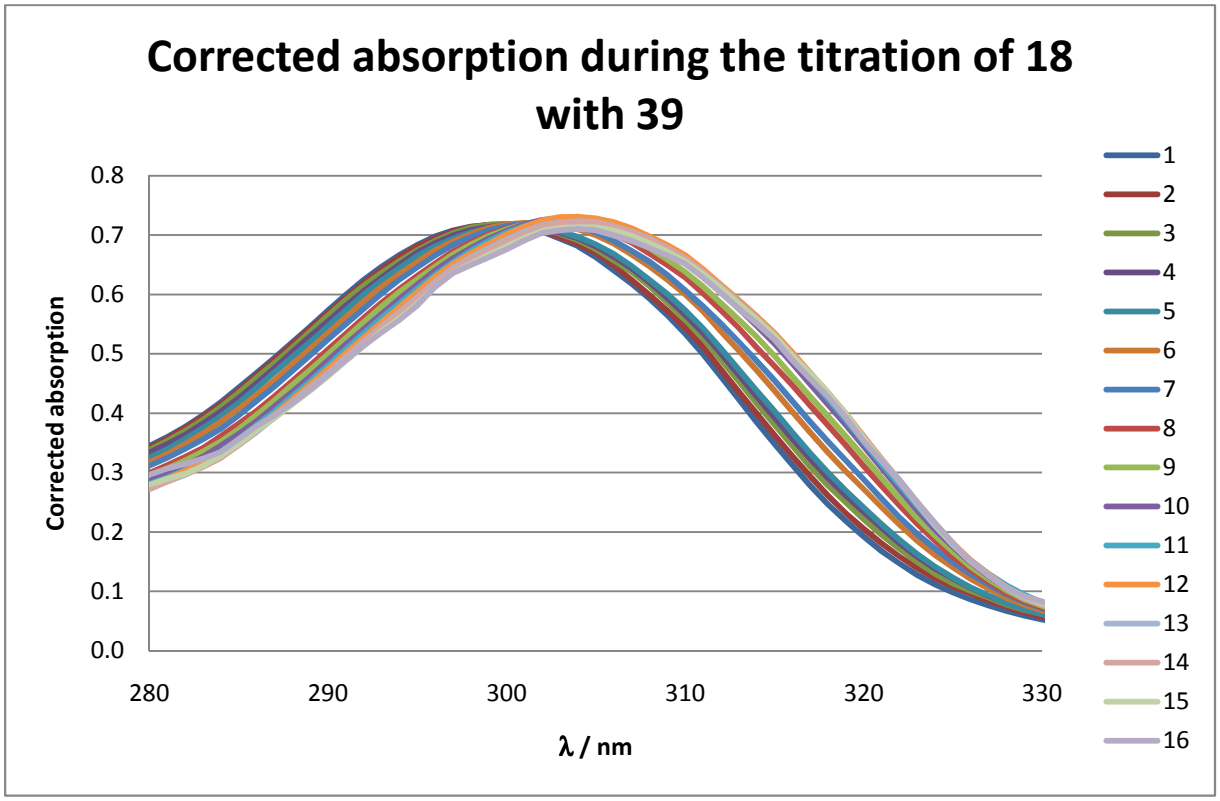

Corrected absorption at 317 nm during the titration of 18 with 36
$A_{corr.}(317)$
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
5
10
15
20
25
n

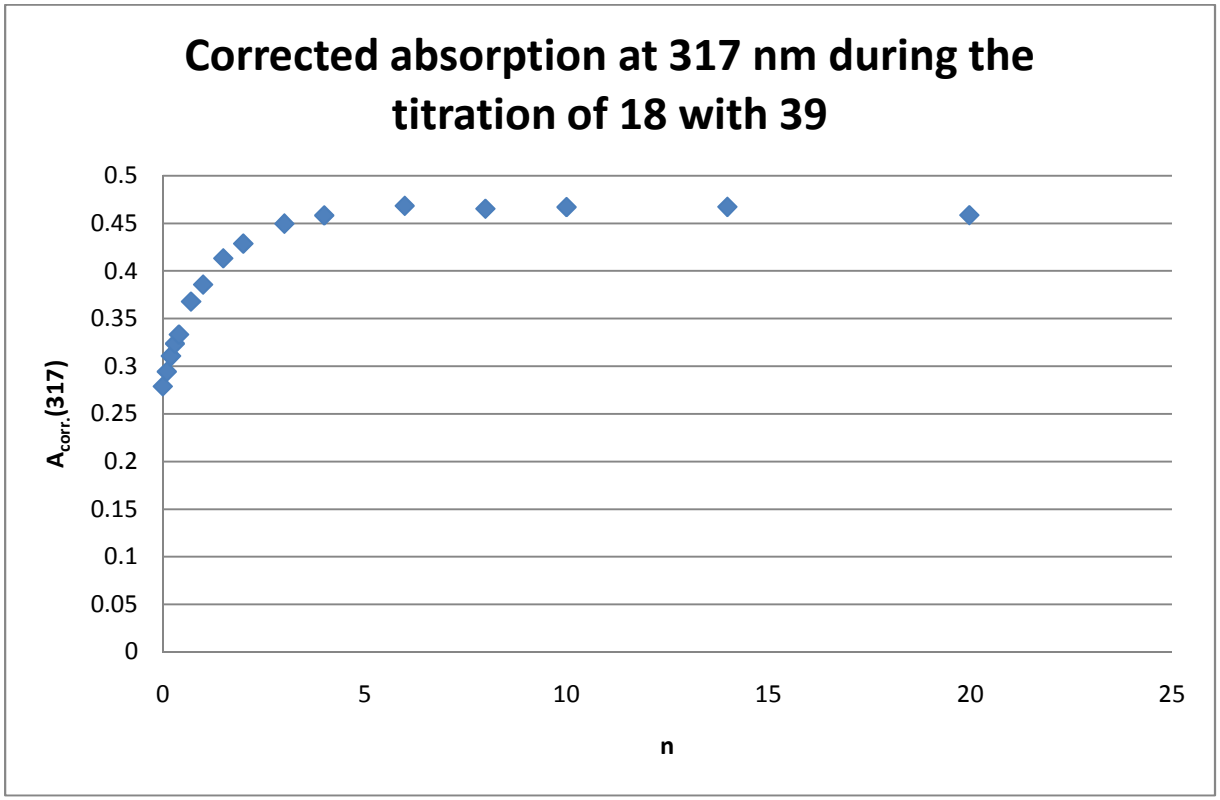

Crude absorption data during the titration of 17 with 39
Absorption
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
220
320
420
520
620
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19


Corrected absorption during the titration of 17 with 39
Corrected Absorption
1.200000
1.000000
0.800000
0.600000
0.400000
0.200000
0.000000
280
290
300
310
320
330
340
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

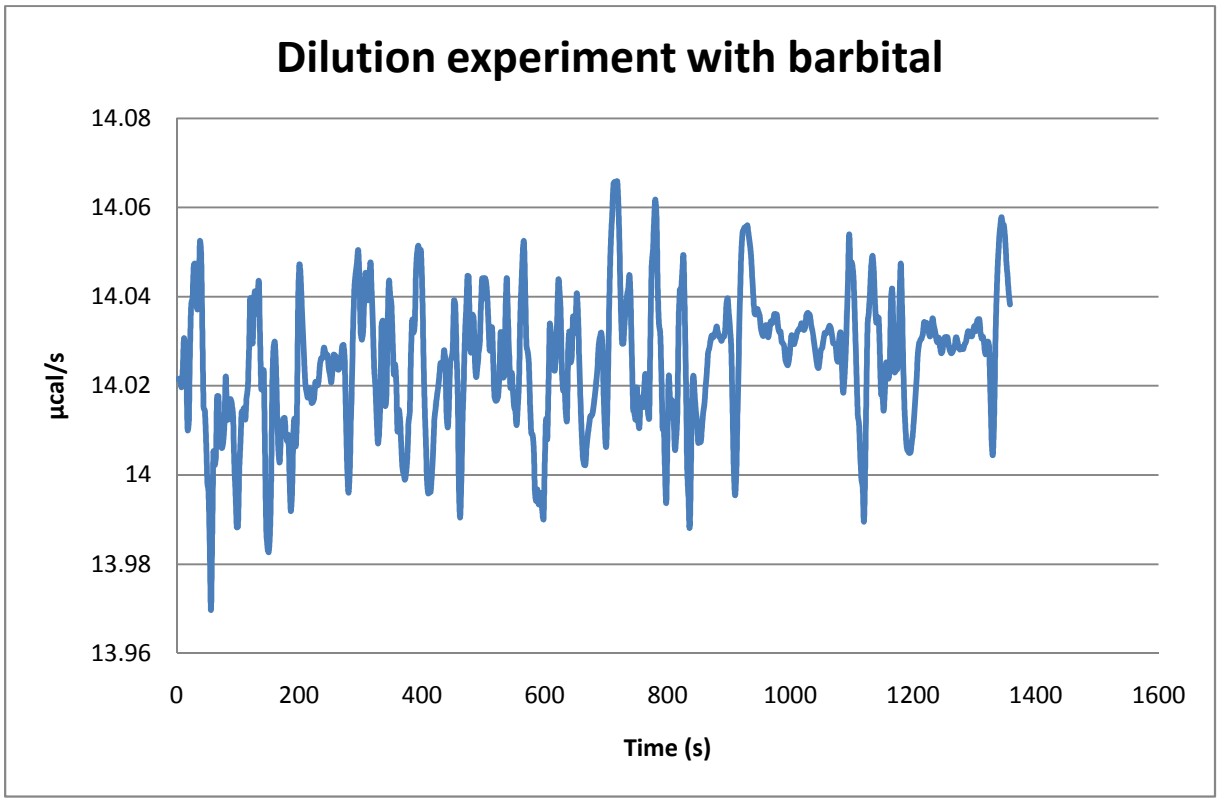

Corrected absorption at 317 nm during the titration of 17 with 39
0.6
0.5
0.4
0.3
0.2
0.1
0
A corr.(317)
0
5
10
15
20
25
n


Crude absorption data during the titration of 18 with 39
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Absorption
220
320
420
520
620
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16


Corrected absorption during the titration of 18 with 39
Corrected absorption
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
280
290
300
310
320
330
λ / nm
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

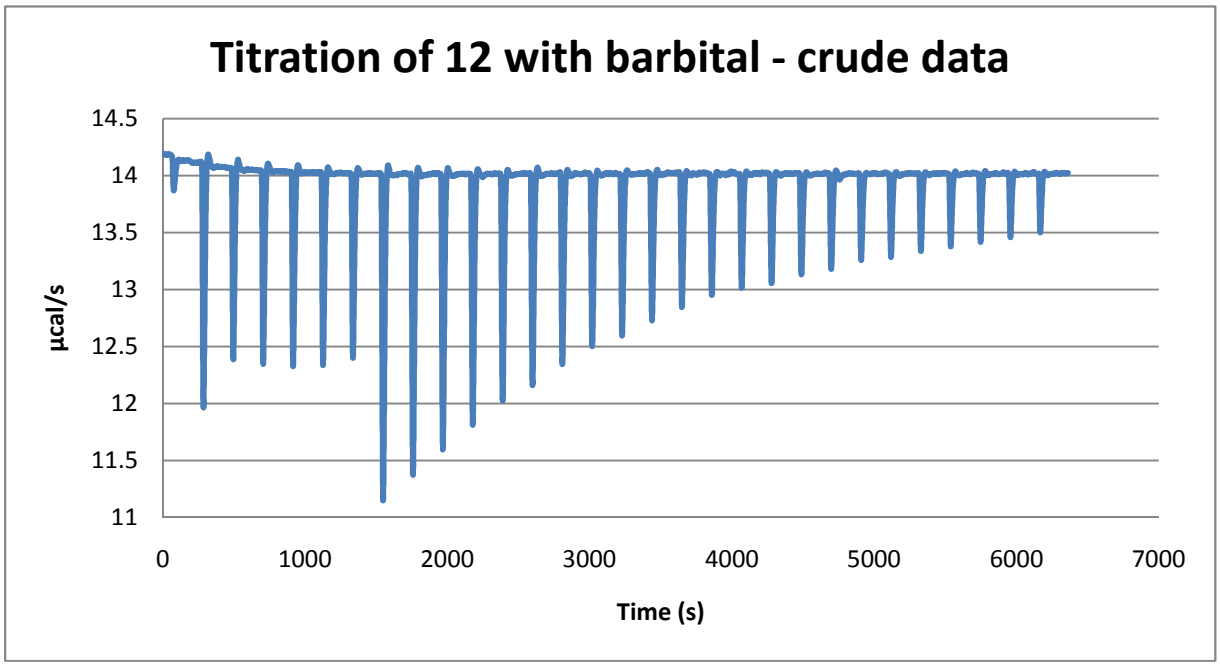

Corrected absorption at 317 nm during the titration of 18 with 39
A corr.(317)
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15
20
25
n

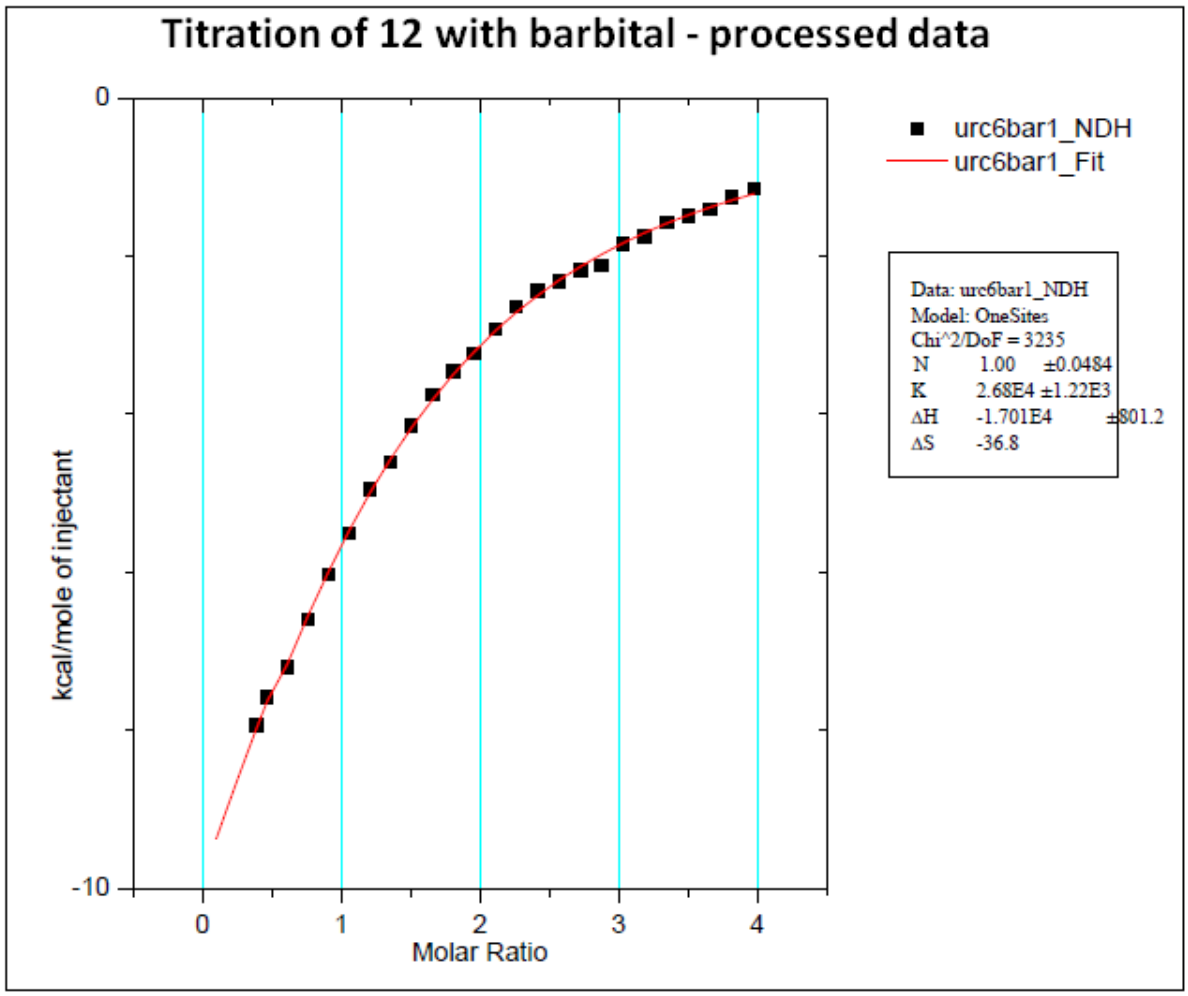
II) ITC data

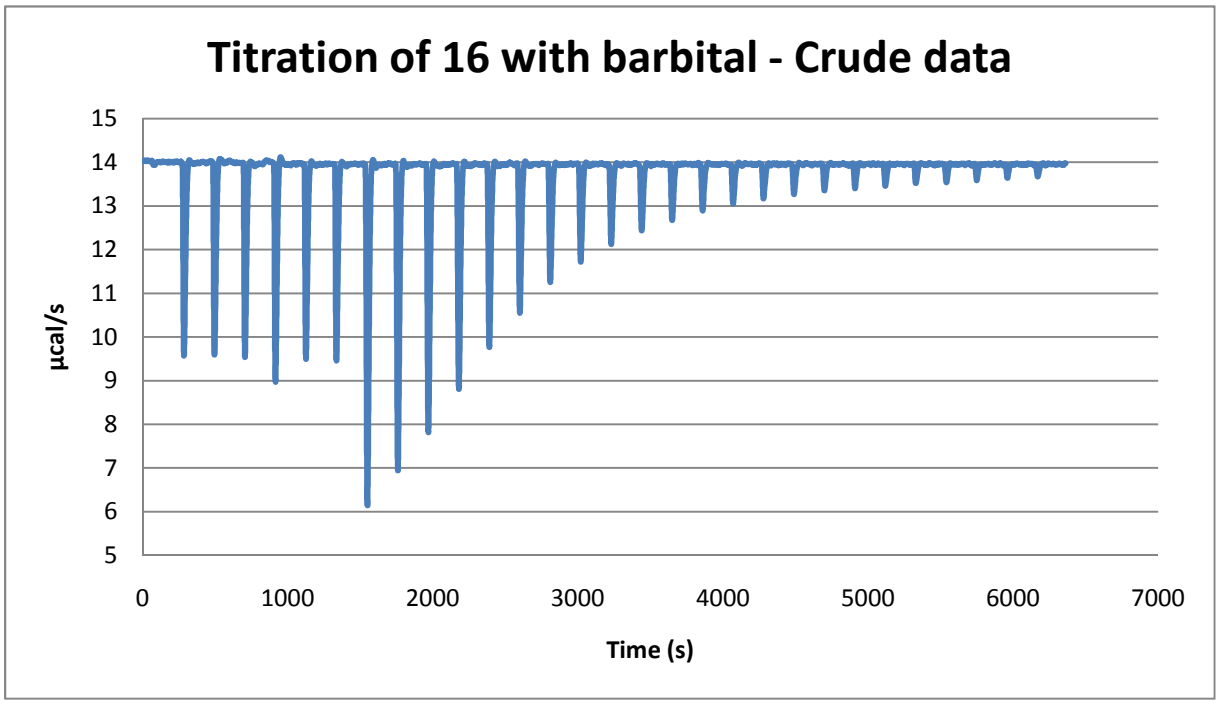


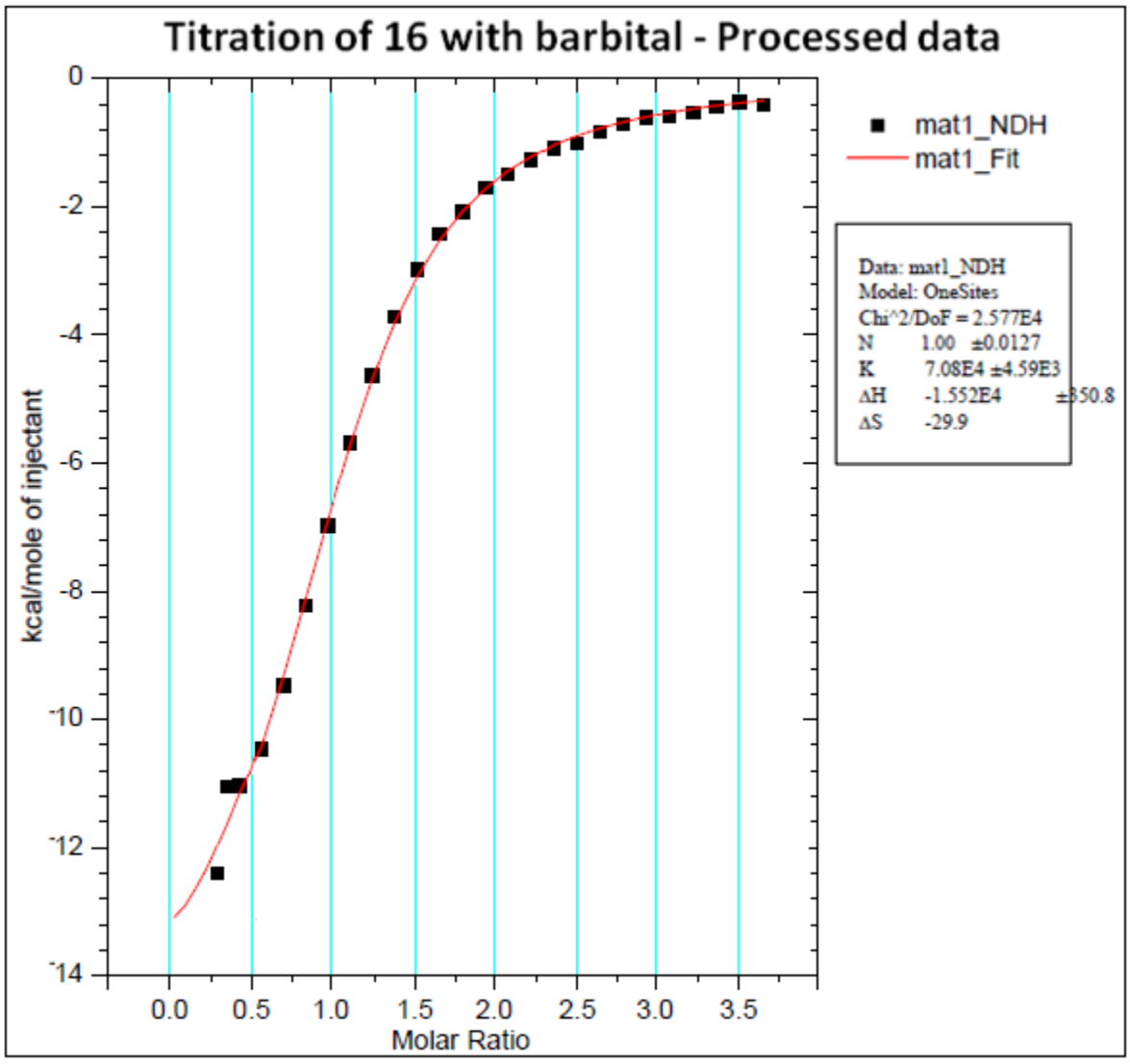
Because only random noise was recorded with barbital, these data were not substracted from the titration data with the different receptors.

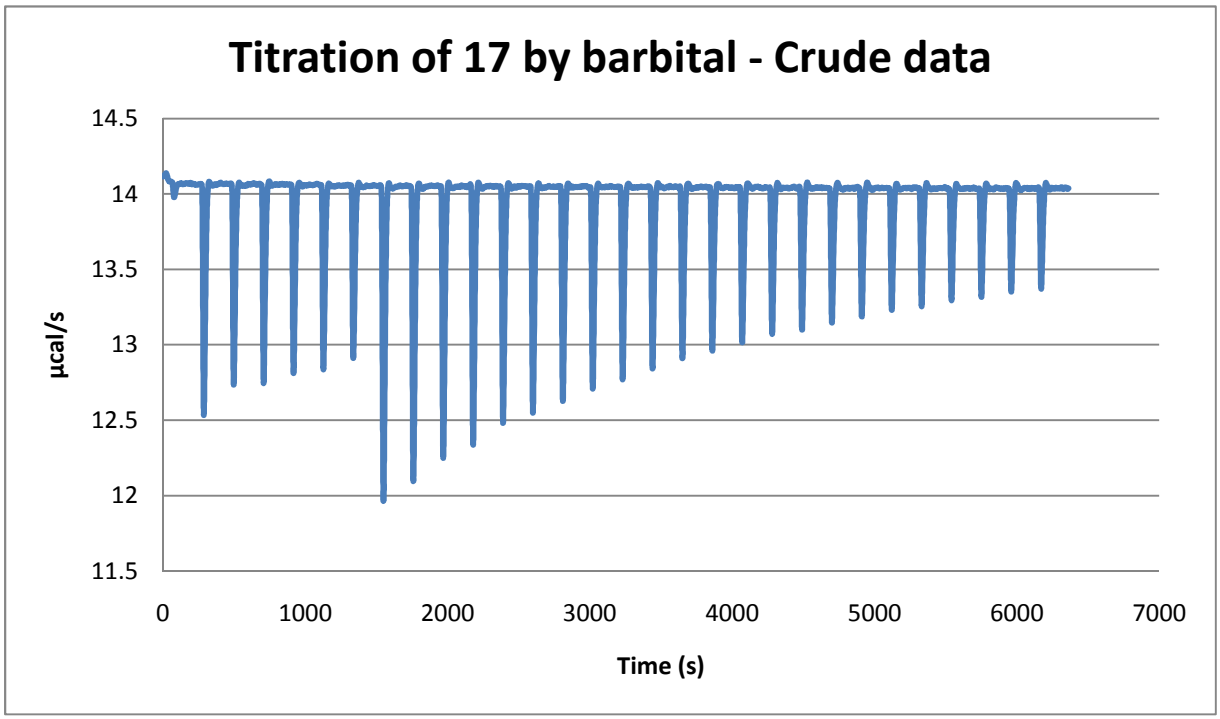
Unless otherwise stated, the following titrations have been made with a starting concentration of the receptor of *0.05 nM*.

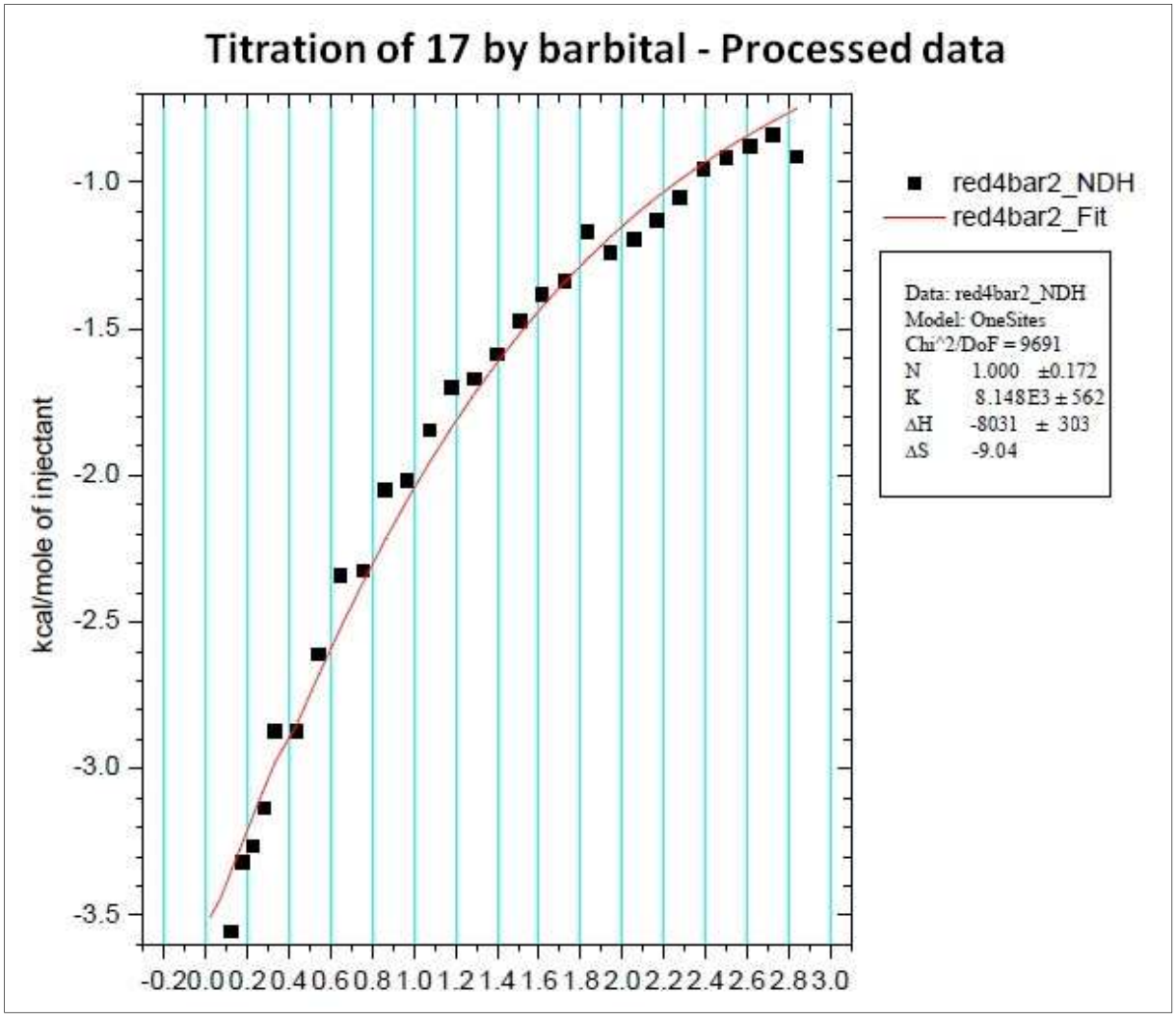

Titration of 12 with barbital - crude data
µcal/s
14.5
14
13.5
13
12.5
12
11.5
11
0
1000
2000
3000
4000
5000
6000
7000
Time (s)

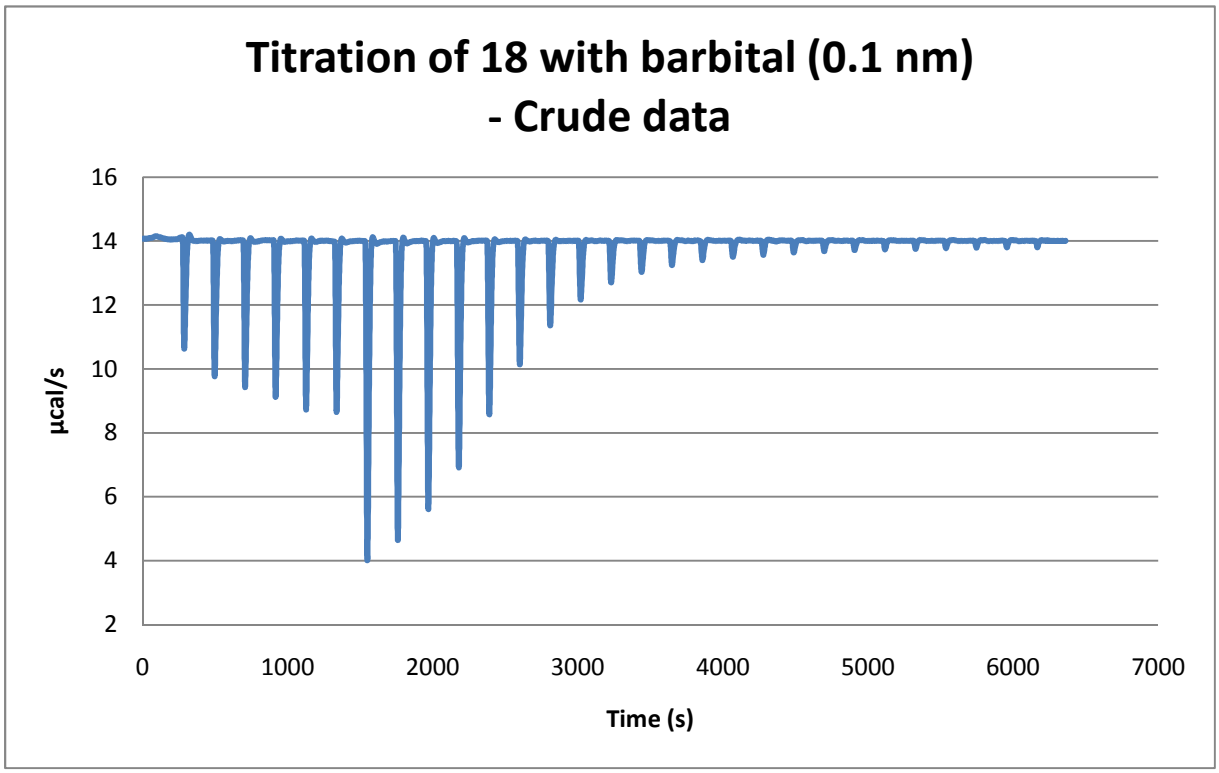

Titration of 12 with barbital - processed data
kcal/mole of injectant
0
-10
0
1
2
3
4
Molar Ratio
urc6bar1_NDH
urc6bar1_Fit
Data: urc6bar1_NDH
Model: OneSites
Chi^2/DoF = 3235
N 1.00 ±0.0484
K 2.68E4 ±1.22E3
ΔH -1.701E4 ±801.2
ΔS -36.8

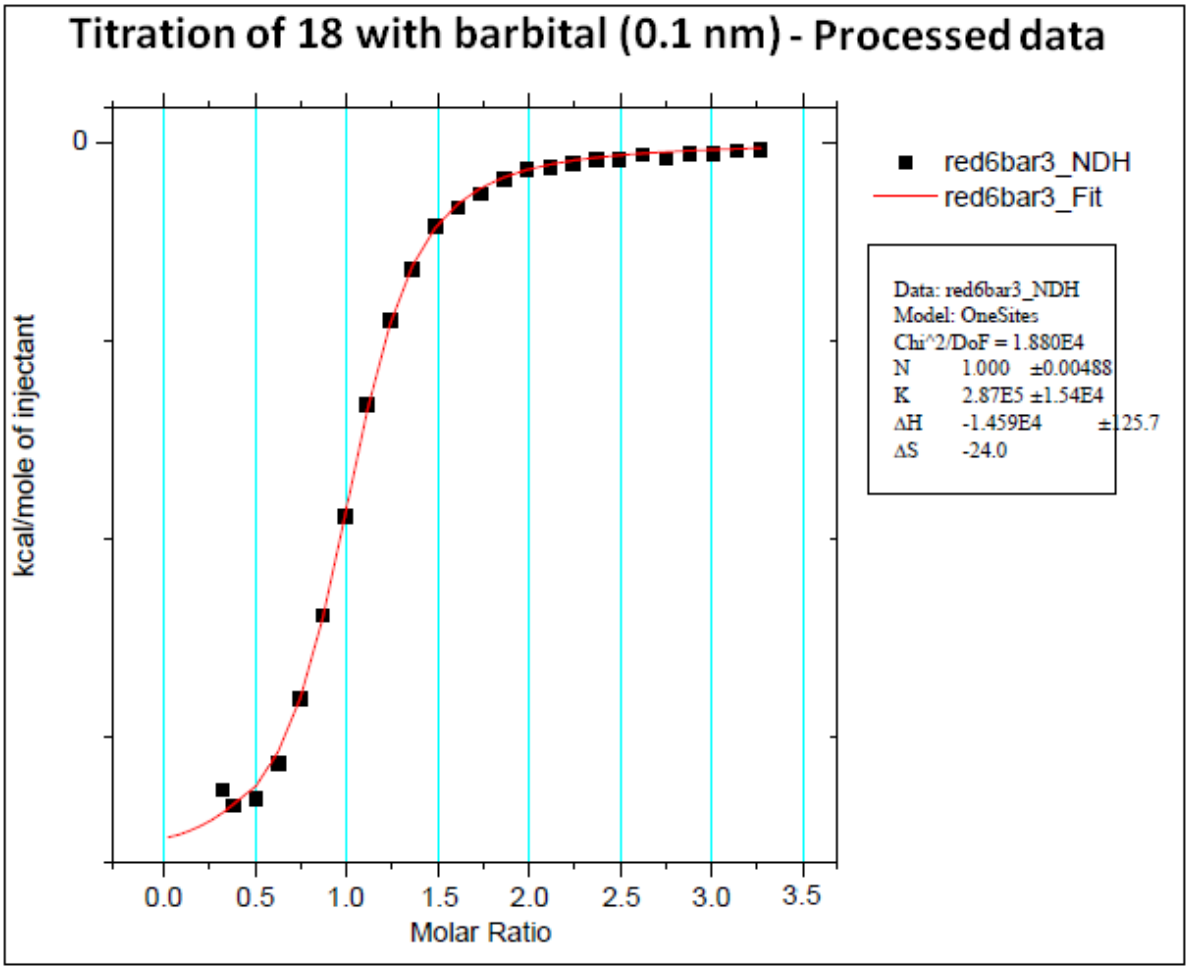

Titration of 16 with barbital - Crude data
µcal/s
15
14
13
12
11
10
9
8
7
6
5
0
1000
2000
3000
4000
5000
6000
7000
Time (s)

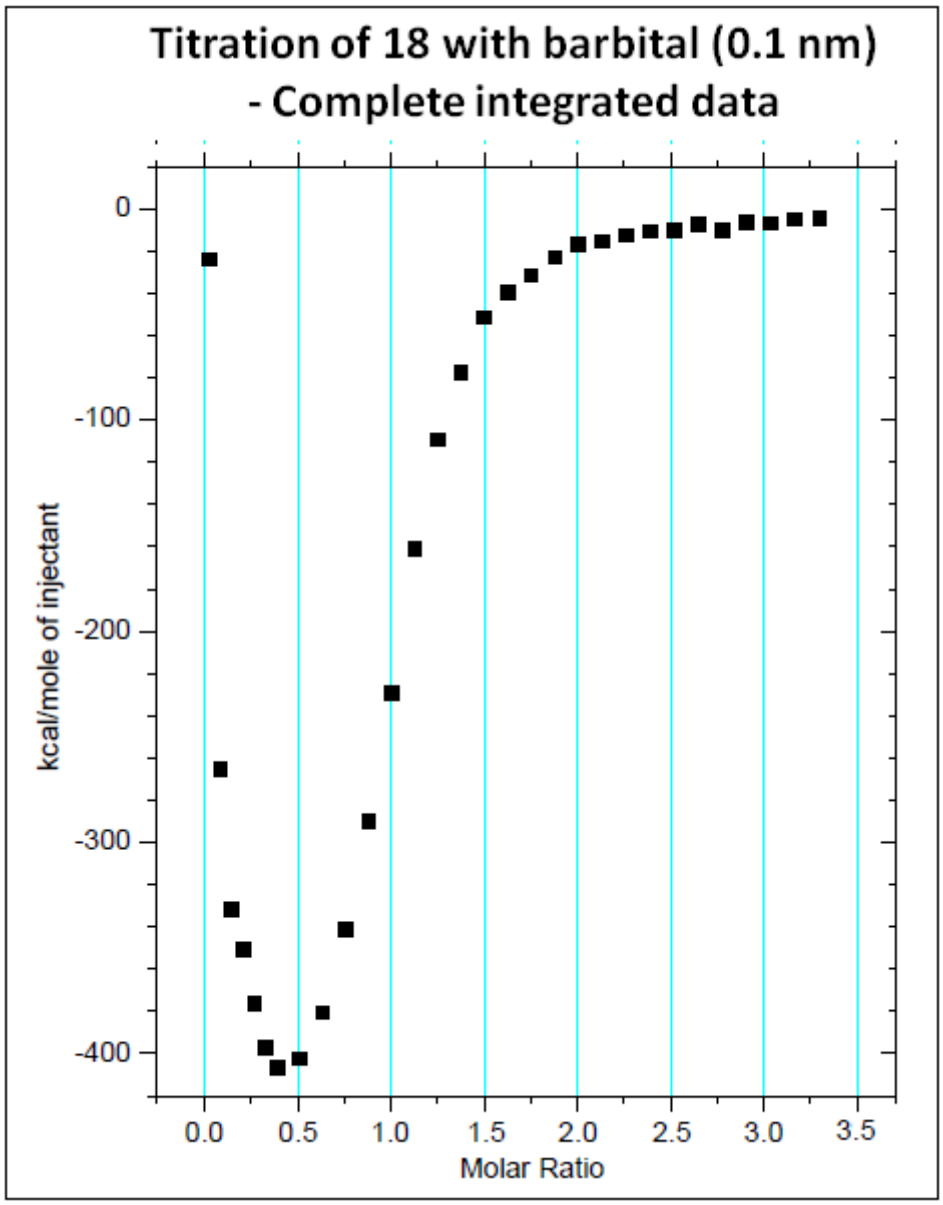

Titration of 16 with barbital - Processed data
kcal/mole of injectant
0
-2
-4
-6
-8
-10
-12
-14
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Molar Ratio
mat1_NDH
mat1_Fit
Data: mat1_NDH
Model: OneSites
Chi^2/DoF = 2.577E4
N 1.00 ±0.0127
K 7.08E4 ±4.59E3
ΔH -1.552E4 ±350.8
ΔS -29.9

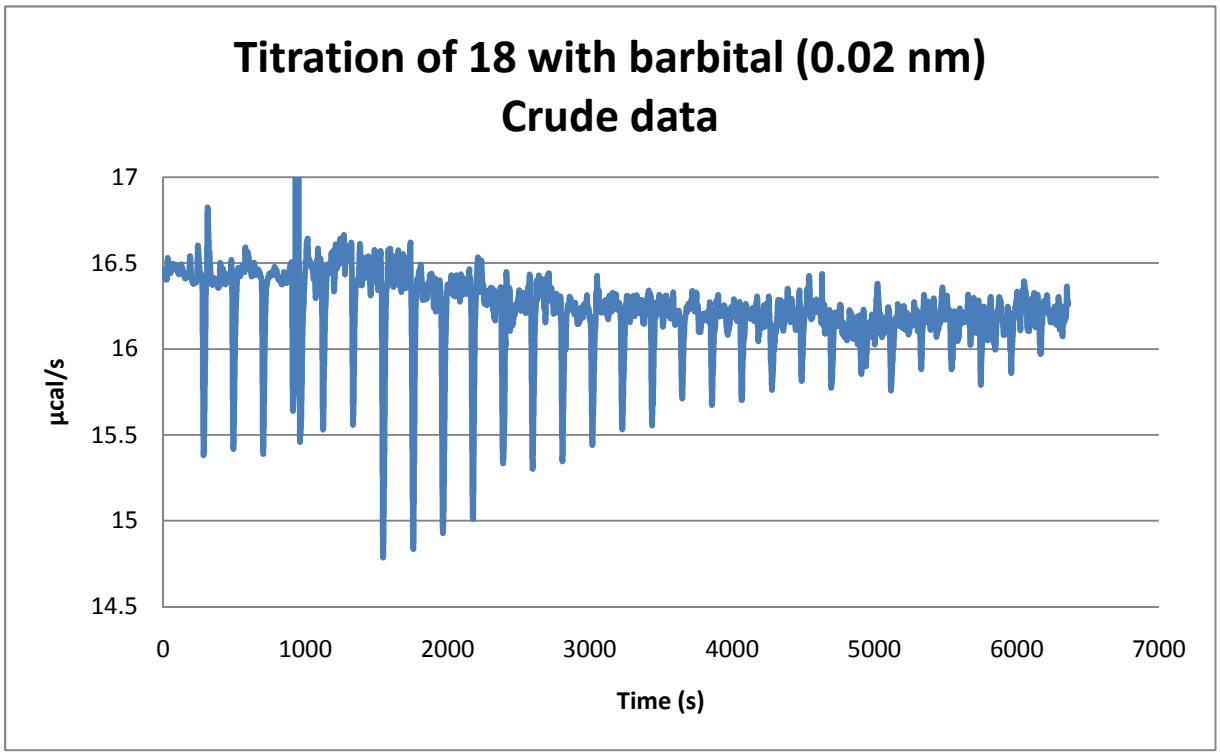

Titration of 17 by barbital - Crude data
µcal/s
14.5
14
13.5
13
12.5
12
11.5
0
1000
2000
3000
4000
5000
6000
7000
Time (s)

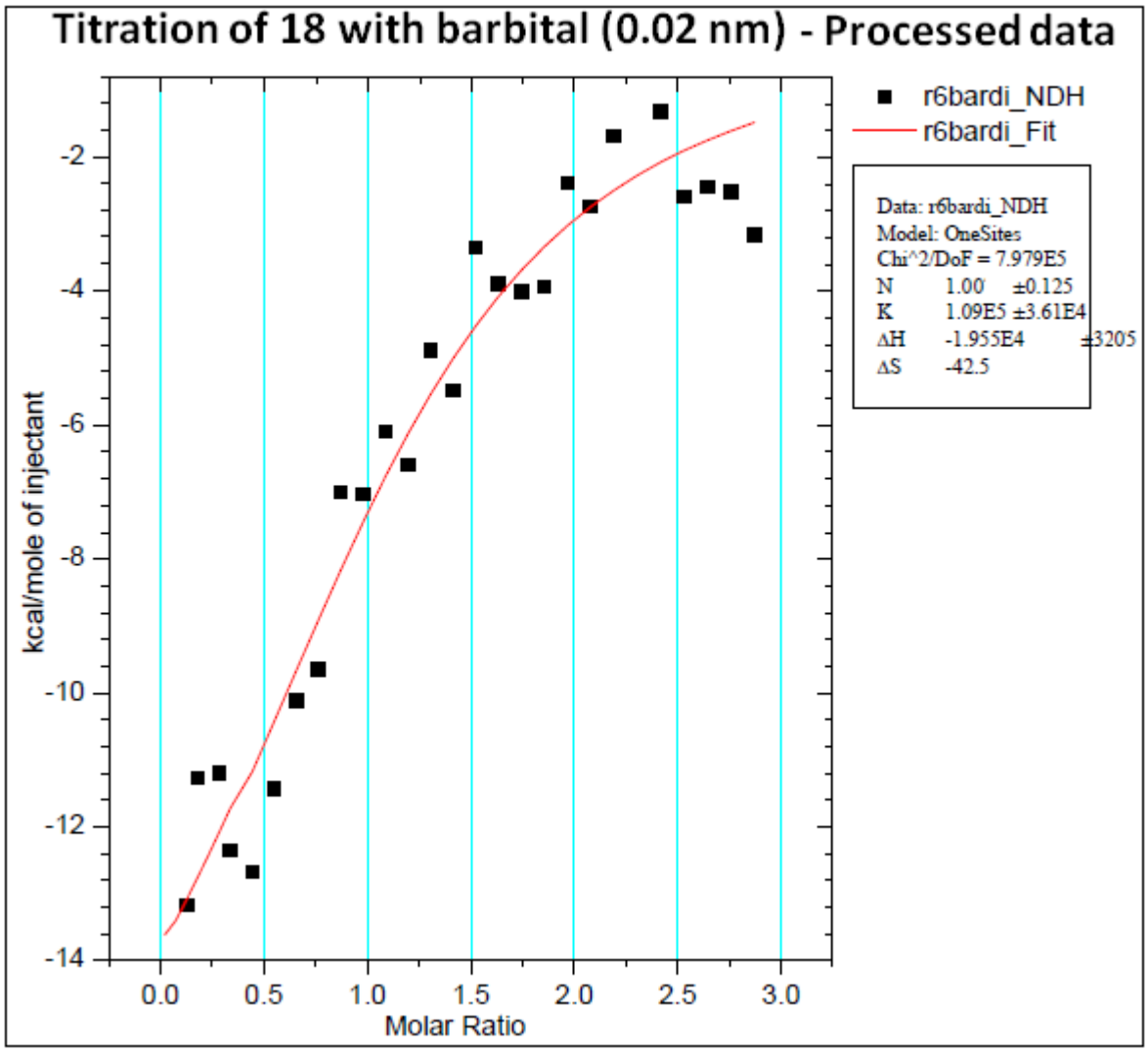

Titration of 17 by barbital - Processed data
kcal/mole of injectant
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-0.2 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0
red4bar2_NDH
red4bar2_Fit
Data: red4bar2_NDH
Model: OneSites
Chi^2/DoF = 9691
N 1.000 ±0.172
K 8.148E3 ± 562
ΔH -8031 ± 303
ΔS -9.04

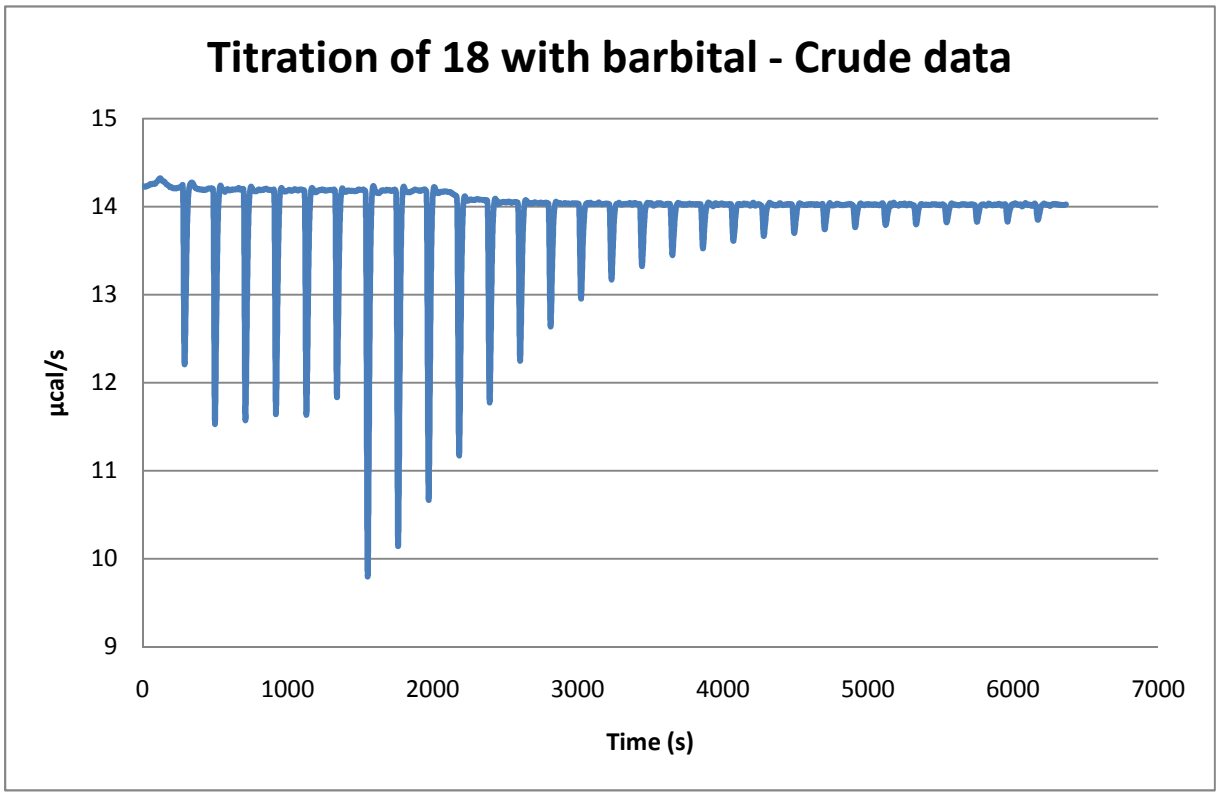

Titration of 18 with barbital (0.1 nm)
- Crude data
µcal/s
16
14
12
10
8
6
4
2
0
1000
2000
3000
4000
5000
6000
7000
Time (s)

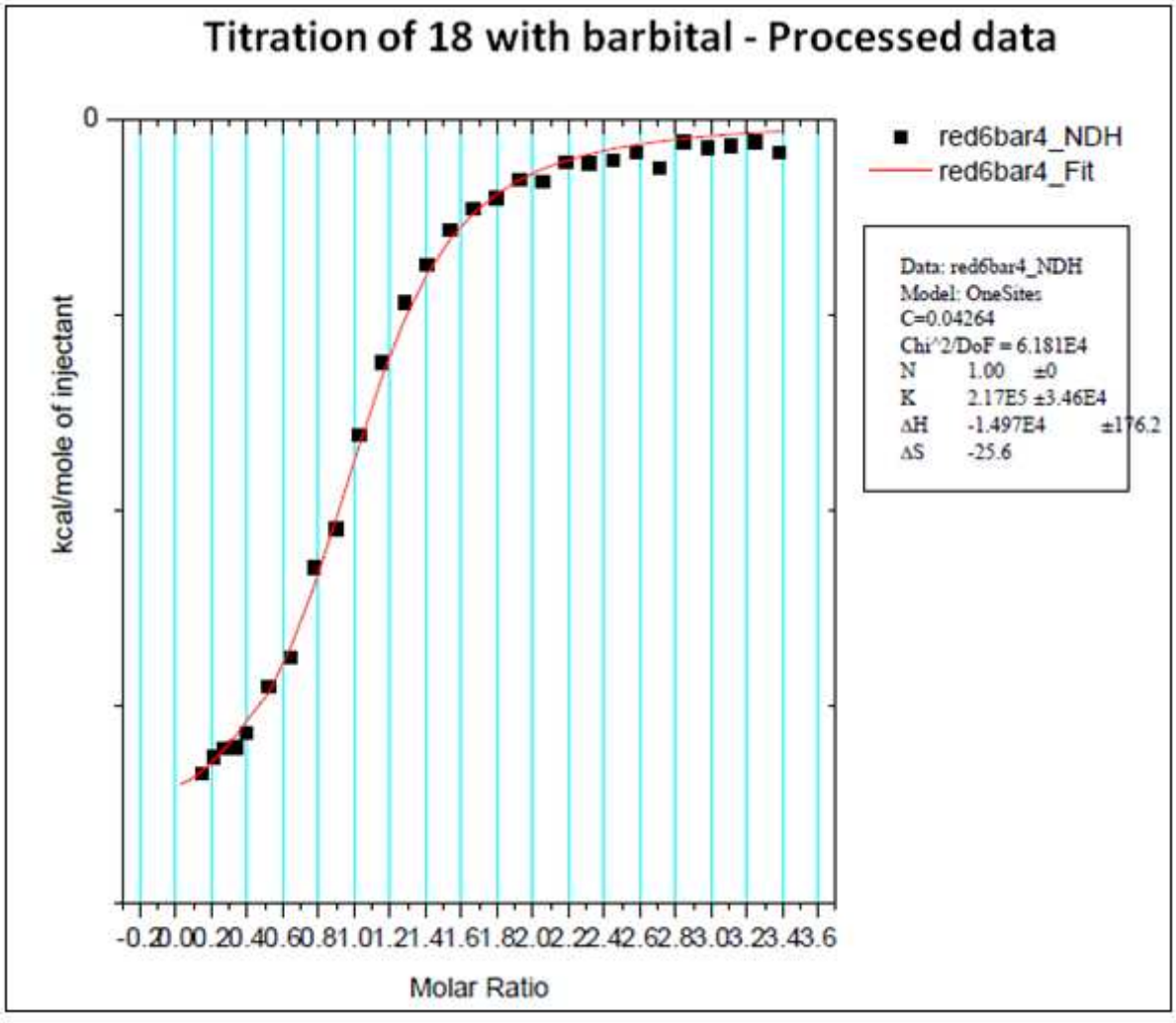

Titration of 18 with barbital (0.1 nm) - Processed data
kcal/mole of injectant
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Molar Ratio
red6bar3_NDH
red6bar3_Fit
Data: red6bar3_NDH
Model: OneSites
Chi^2/DoF = 1.880E4
N 1.000 ±0.00488
K 2.87E5 ±1.54E4
ΔH -1.459E4 ±125.7
ΔS -24.0

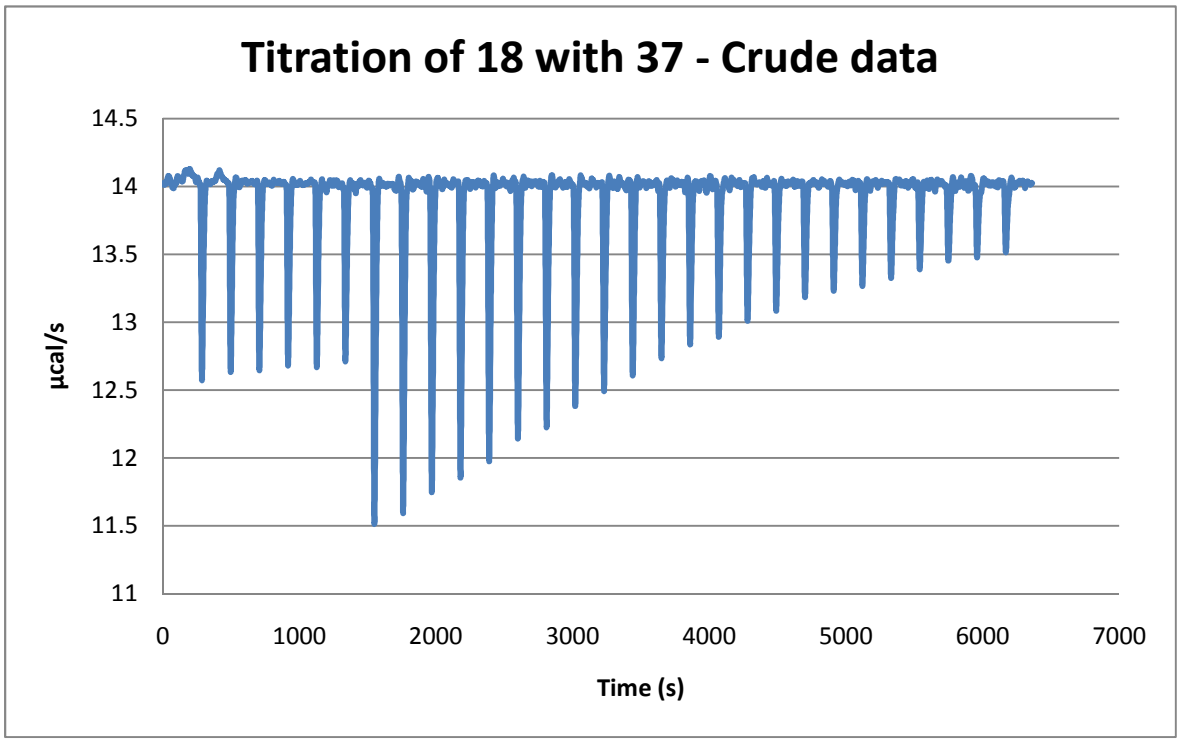

Titration of 18 with barbital (0.1 nm)
- Complete integrated data
kcal/mole of injectant
0
-100
-200
-300
-400
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Molar Ratio

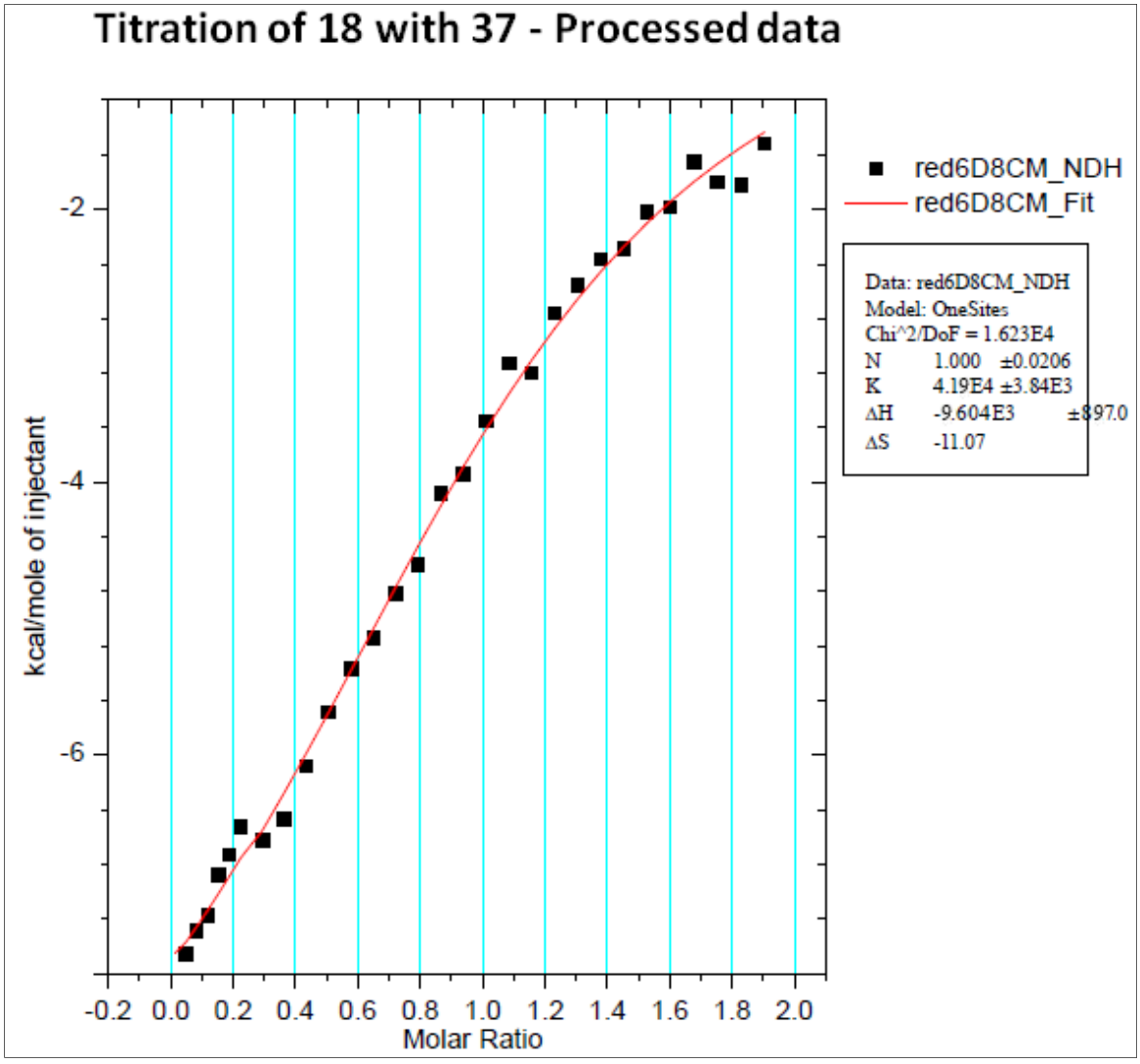

Titration of 18 with barbital (0.02 nm)
Crude data
µcal/s
17
16.5
16
15.5
15
14.5
0
1000
2000
3000
4000
5000
6000
7000
Time (s)

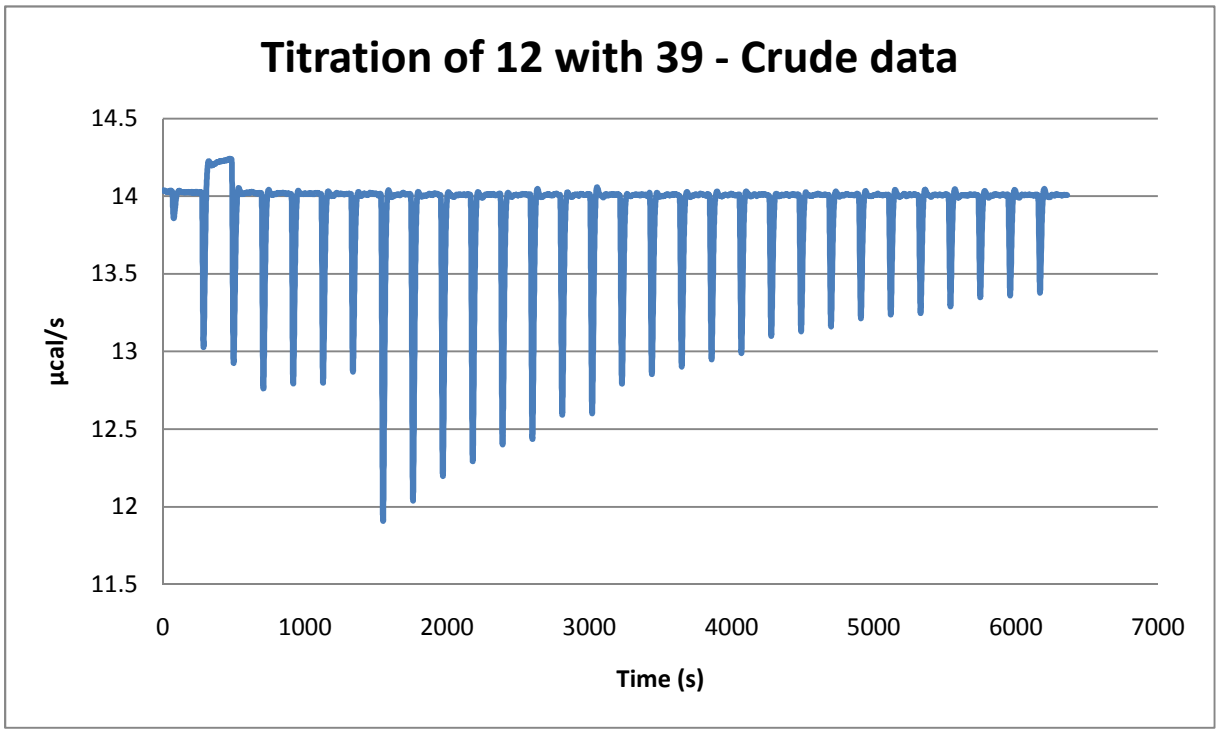

Titration of 18 with barbital (0.02 nm) - Processed data
r6bardi_NDH
r6bardi_Fit
Data: r6bardi_NDH
Model: OneSites
Chi^2/DoF = 7.979E5
N 1.00 ±0.125
K 1.09E5 ±3.61E4
ΔH -1.955E4 ±3205
ΔS -42.5
kcal/mole of injectant
-2
-4
-6
-8
-10
-12
-14
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Molar Ratio

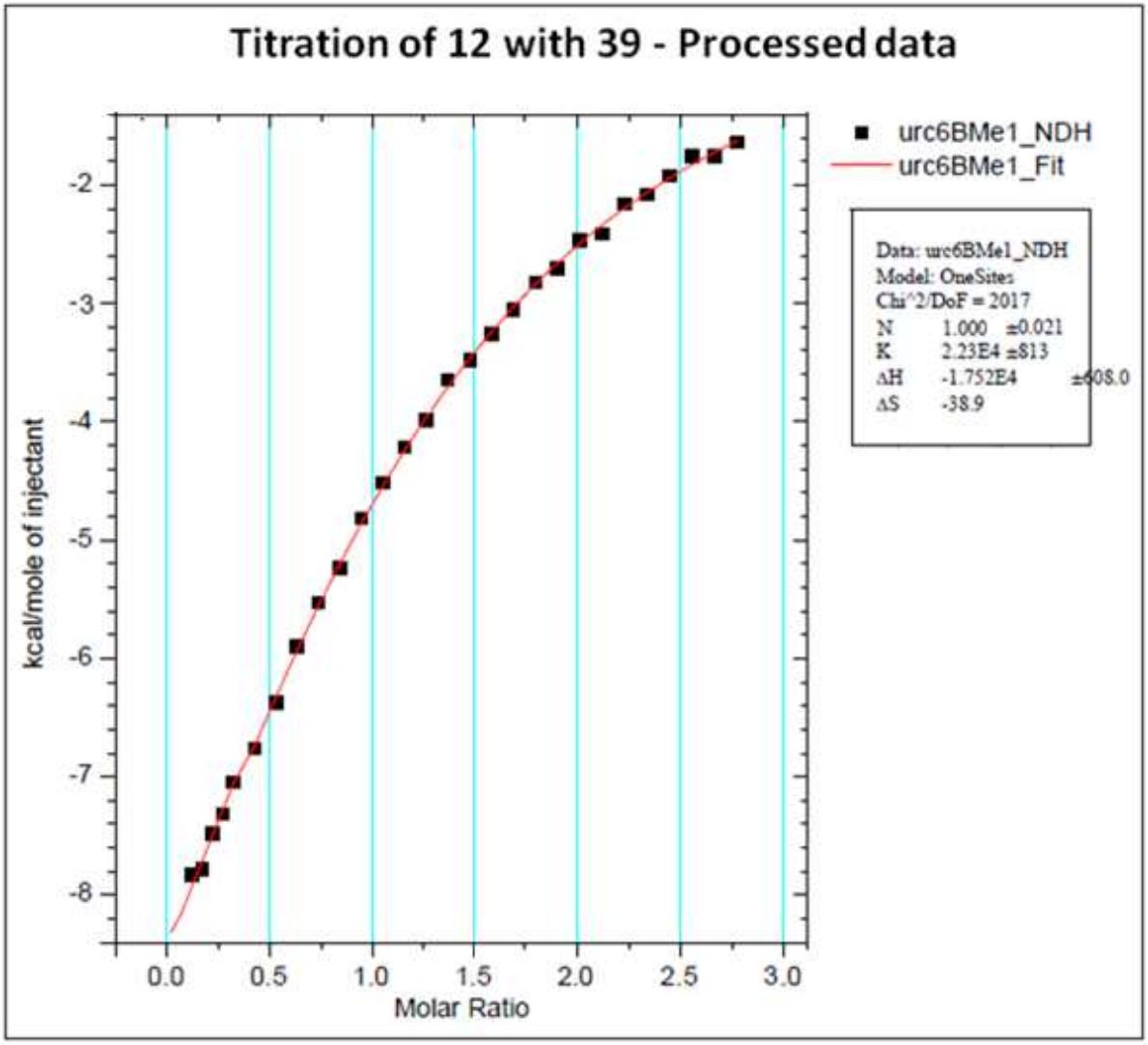

Titration of 18 with barbital - Crude data
µcal/s
15
14
13
12
11
10
9
0
1000
2000
3000
4000
5000
6000
7000
Time (s)

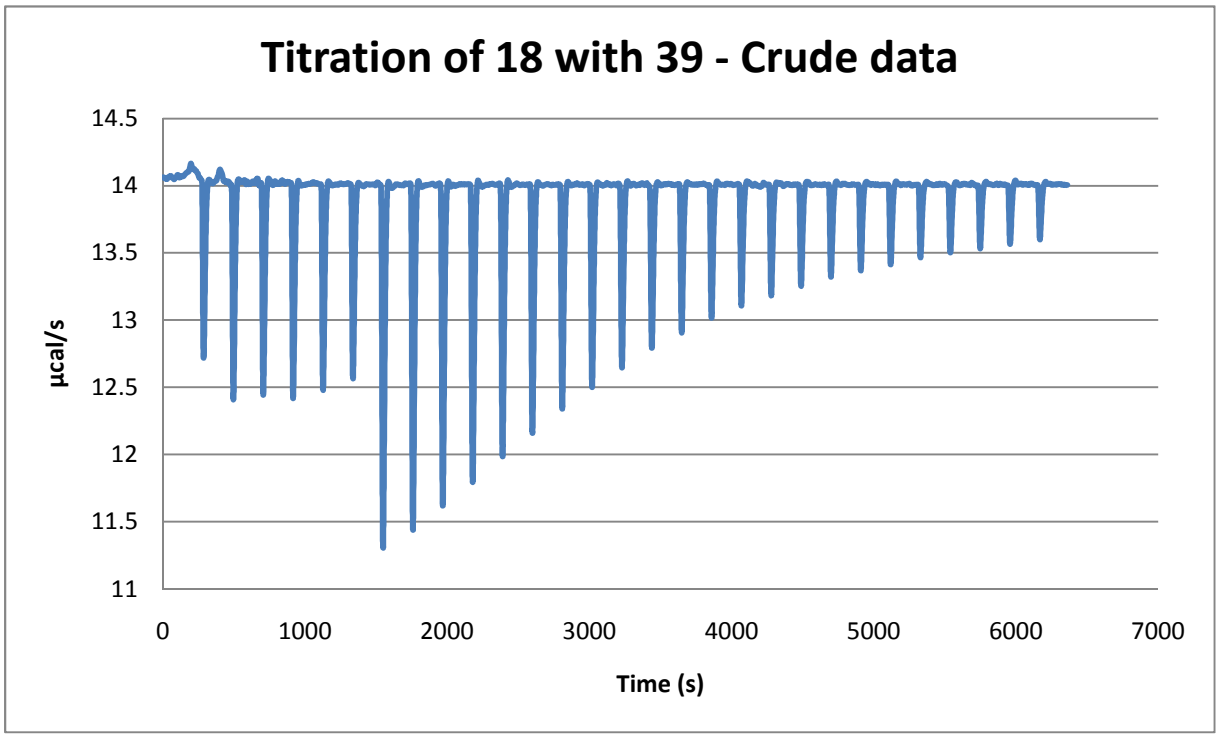

Titration of 18 with barbital - Processed data
kcal/mole of injectant
0
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
Molar Ratio
red6bar4_NDH
red6bar4_Fit
Data: red6bar4_NDH
Model: OneSites
C=0.04264
Chi^2/DoF = 6.181E4
N 1.00 ±0
K 2.17E5 ±3.46E4
ΔH -1.497E4 ±176.2
ΔS -25.6

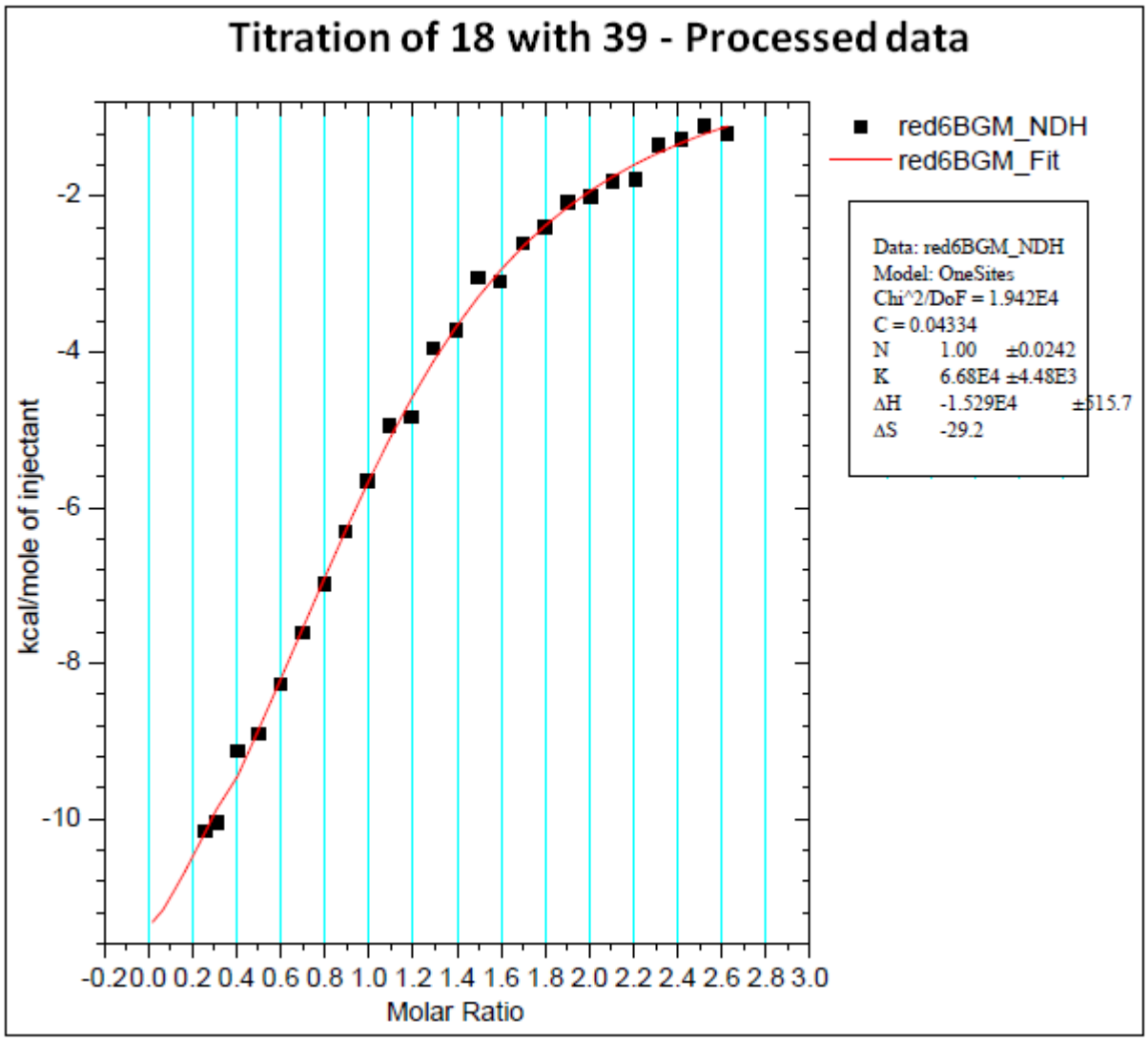

Titration of 18 with 37 - Crude data
µcal/s
14.5
14
13.5
13
12.5
12
11.5
11
0
1000
2000
3000
4000
5000
6000
7000
Time (s)

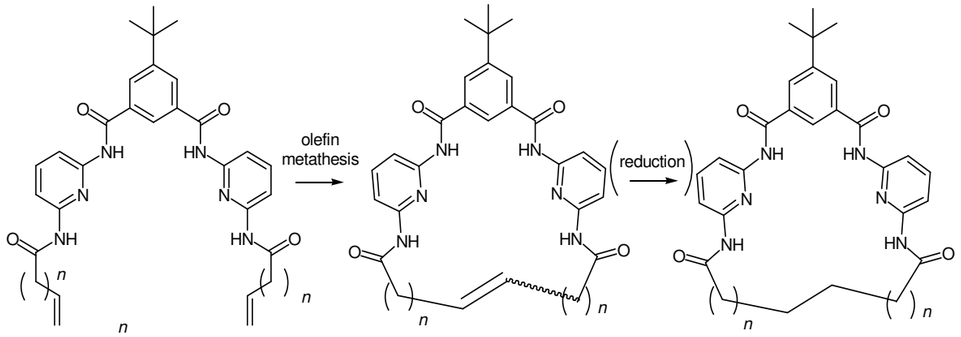

Titration of 18 with 37 - Processed data
kcal/mole of injectant
-2
-4
-6
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Molar Ratio
red6D8CM_NDH
red6D8CM_Fit
Data: red6D8CM_NDH
Model: OneSites
Chi^2/DoF = 1.623E4
N 1.000 ±0.0206
K 4.19E4 ±3.84E3
ΔH -9.604E3 ±897.0
ΔS -11.07


Titration of 12 with 39 - Crude data
µcal/s
14.5
14
13.5
13
12.5
12
11.5
0
1000
2000
3000
4000
5000
6000
7000
Time (s)


Titration of 12 with 39 - Processed data
urc6BMe1_NDH
urc6BMe1_Fit
Data: urc6BMe1_NDH
Model: OneSites
Chi^2/DoF = 2017
N 1.000 ±0.021
K 2.23E4 ±813
ΔH -1.752E4 ±608.0
ΔS -38.9
kcal/mole of injectant
-2
-3
-4
-5
-6
-7
-8
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Molar Ratio


Titration of 18 with 39 - Crude data
µcal/s
14.5
14
13.5
13
12.5
12
11.5
11
0
1000
2000
3000
4000
5000
6000
7000
Time (s)

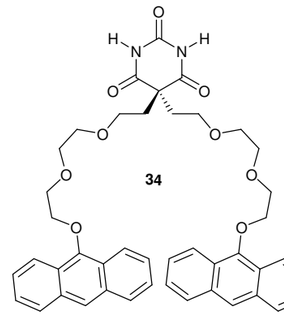

Titration of 18 with 39 - Processed data
kcal/mole of injectant
-2
-4
-6
-8
-10
-0.2 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0
Molar Ratio
red6BGM_NDH
red6BGM_Fit
Data: red6BGM_NDH
Model: OneSites
Chi^2/DoF = 1.942E4
C = 0.04334
N 1.00 ±0.0242
K 6.68E4 ±4.48E3
ΔH -1.529E4 ±515.7
ΔS -29.2



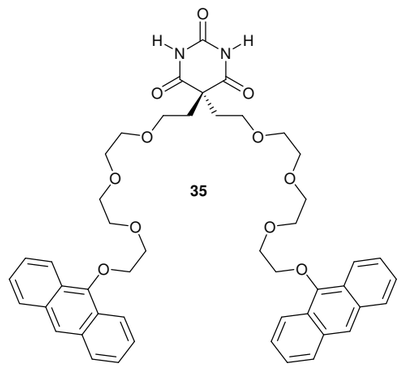
n	
2	**9**
4	**10**
5	**11**
6	**12**
8	**13**

n	
4	**14**
6	**15**
8	**16**

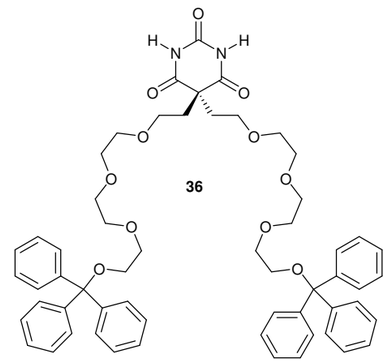
n	
4	**17**
6	**18**



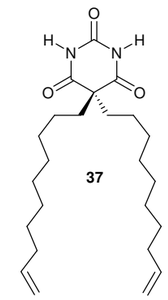
34



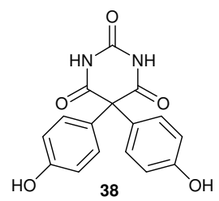
35



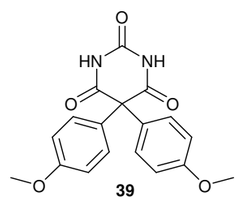
36



37



38



39