Supplementary Informations

Calix[4]phyrin based redox architectures: towards new molecular tools for electrochemical sensing.

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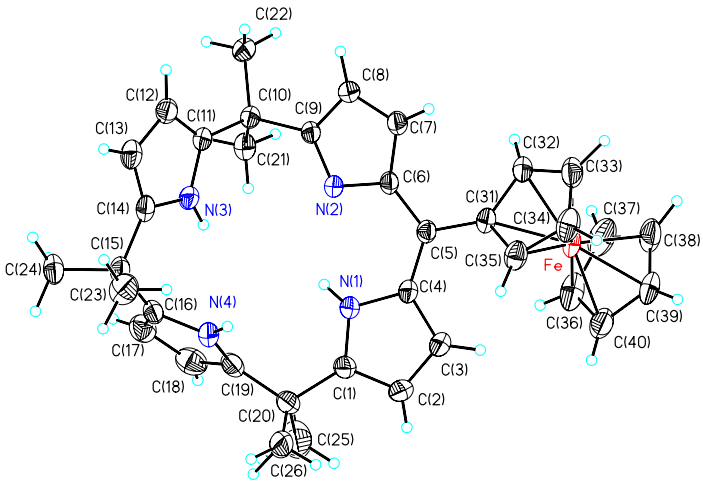
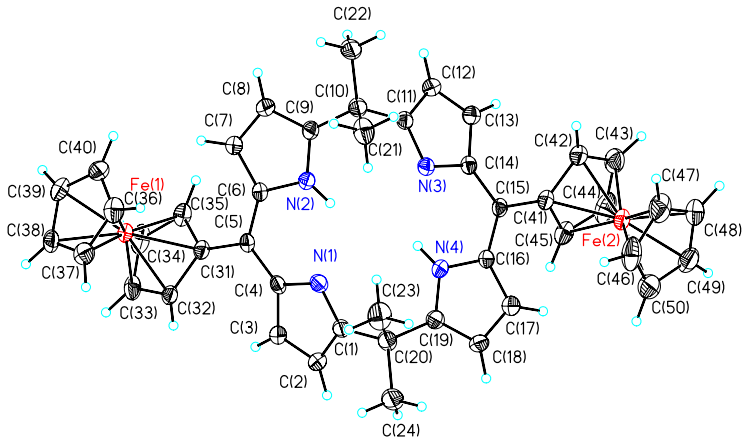
Table 1. Crystal data and structure refinement for struc. 1



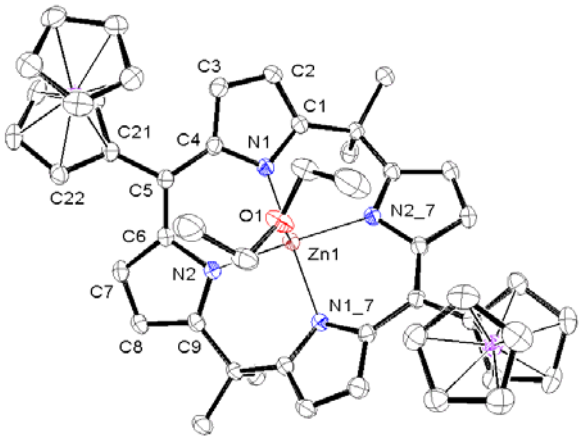
Empirical formula	C40 H46 Fe N4 O
Formula weight	654.66
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 7.7327(15) A alpha = 108.78(3) deg. b = 13.530(3) A beta = 91.96(3) deg. c = 17.245(3) A gamma = 91.09(3) deg.
Volume, Z	1706.3(6) A^3, 2
Density (calculated)	1.274 Mg/m^3
Absorption coefficient	0.479 mm^-1
F(000)	696
Crystal size	0.50 x 0.20 x 0.20 mm
Theta range for data collection	2.32 to 28.76 deg.
Limiting indices	-10<=h<=10, -17<=k<=17, -18<=l<=23
Reflections collected	10819
Independent reflections	7633 [R(int) = 0.0176]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7633 / 0 / 415
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0493, wR2 = 0.1277
R indices (all data)	R1 = 0.0676, wR2 = 0.1390
Largest diff. peak and hole	0.477 and -0.287 e.A^-3

Table 2. Crystal data and structure refinement for struc 2



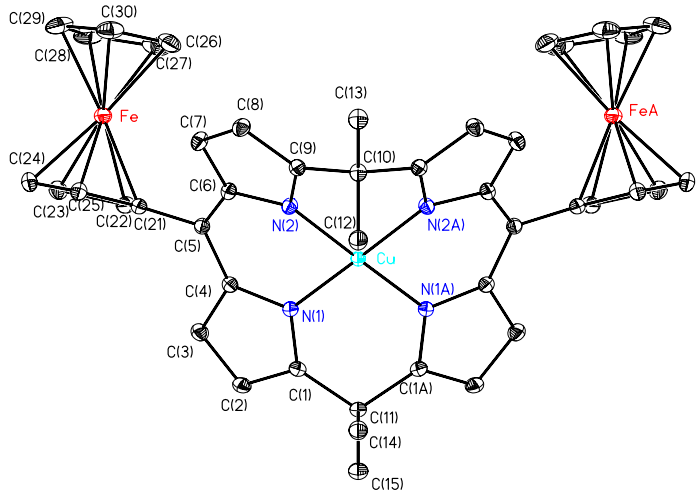
Empirical formula	C46 H42 Cl6 Fe2 N4
Formula weight	975.24
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 12.671(3) A alpha = 90 deg. b = 11.944(2) A beta = 112.22(3) deg. c = 15.545(3) A gamma = 90 deg.
Volume, Z	2178.1(8) A^3, 2
Density (calculated)	1.487 Mg/m^3
Absorption coefficient	1.073 mm^-1
F(000)	1000
Crystal size	0.50 x 0.20 x 0.20 mm
Theta range for data collection	1.42 to 28.90 deg.
Limiting indices	-16<=h<=13, -15<=k<=14, -17<=l<=20
Reflections collected	13871
Independent reflections	8981 [R(int) = 0.0160]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8981 / 4 / 556
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0435, wR2 = 0.1063
R indices (all data)	R1 = 0.0525, wR2 = 0.1141
Absolute structure parameter	0.027(14)
Largest diff. peak and hole	0.453 and -0.354 e.A^-3

Table 3. Crystal data and structure refinement for struc 4



Empirical formula	C48 H48 Fe2 N4 O Zn
Formula weight	873.97
Temperature	223(2) K
Wavelength	0.71073 A
Crystal system	Tetragonal
Space group	P4(1)2(1)2
Unit cell dimensions	a = 10.7004(15) A alpha = 90 deg. b = 10.7004(15) A beta = 90 deg. c = 34.398(7) A gamma = 90 deg.
Volume, Z	3938.6(11) A^3, 4
Density (calculated)	1.474 Mg/m^3
Absorption coefficient	1.374 mm^-1
F(000)	1816
Crystal size	0.30 x 0.15 x 0.08 mm
Theta range for data collection	1.99 to 28.99 deg.
Limiting indices	-12<=h<=14, -13<=k<=13, -21<=l<=46
Reflections collected	16132
Independent reflections	4838 [R(int) = 0.0214]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4838 / 0 / 255
Goodness-of-fit on F^2	1.162
Final R indices [I>2sigma(I)]	R1 = 0.0312, wR2 = 0.0719
R indices (all data)	R1 = 0.0342, wR2 = 0.0727
Absolute structure parameter	0.027(13)
Largest diff. peak and hole	0.301 and -0.500 e.A^-3

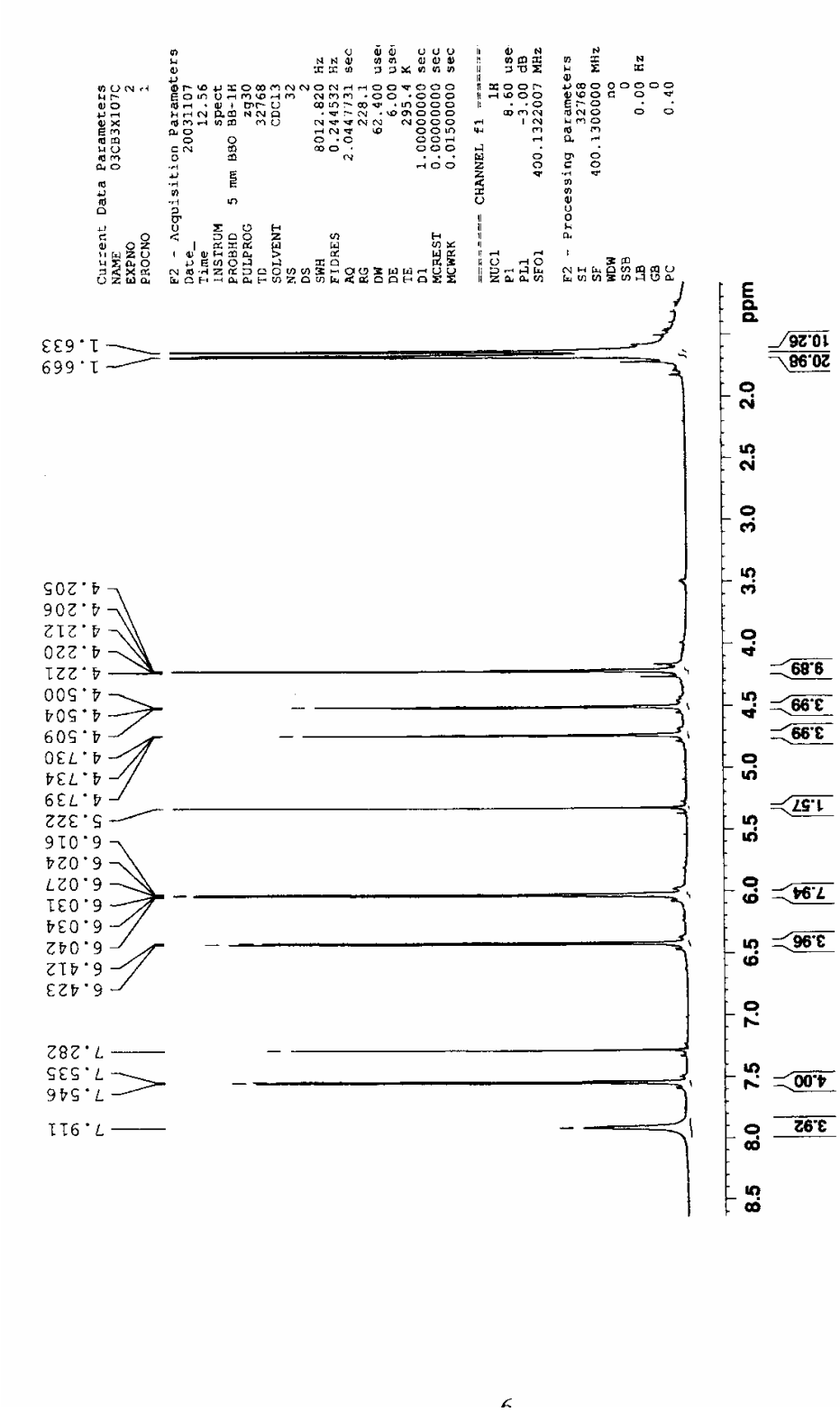
Table 4. Crystal data and structure refinement for struc 5.



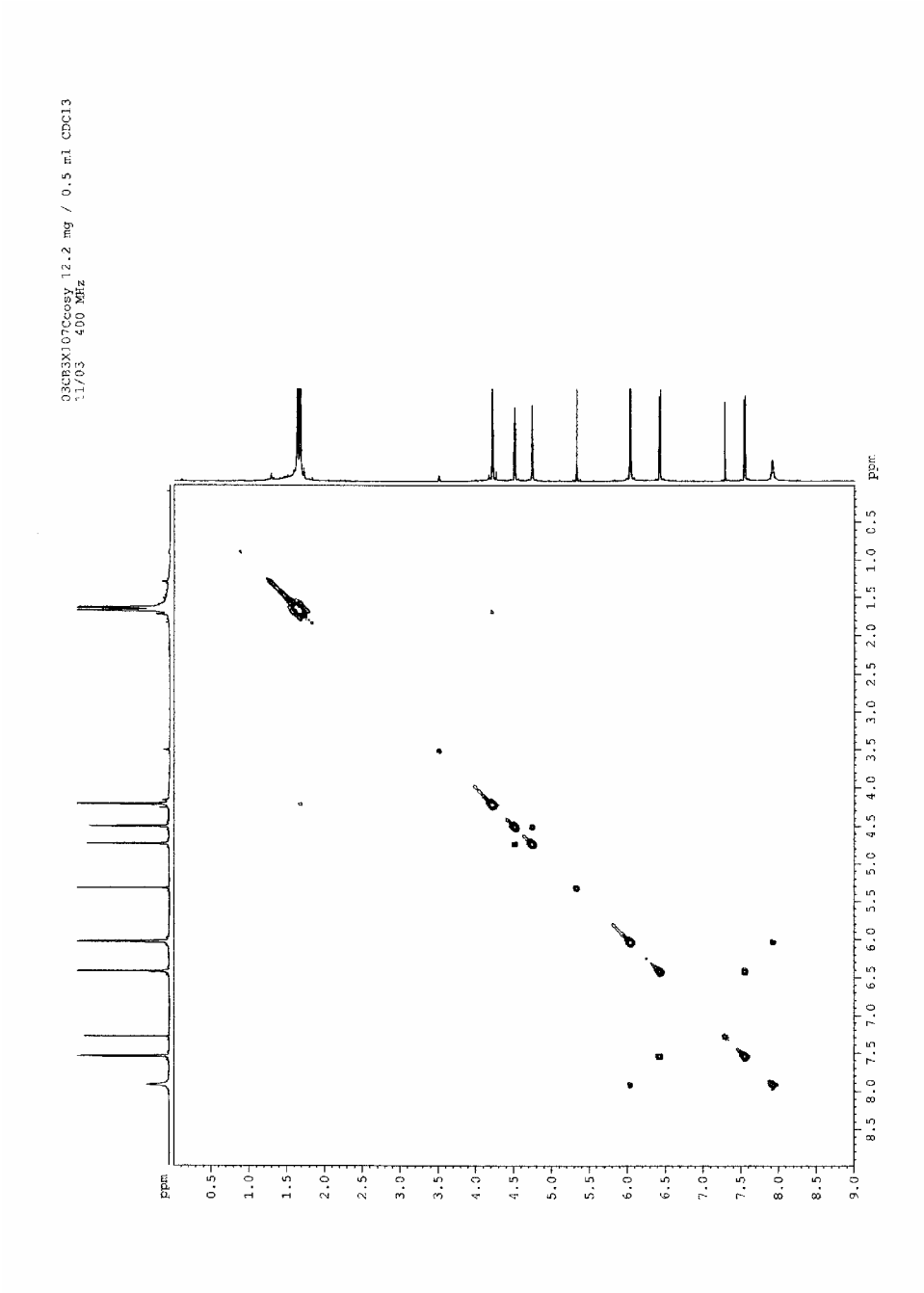
Empirical formula	C45 H40 Cl2 Cu Fe2 N4
Formula weight	882.95
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Orthorhombic
Space group	Pnma
Unit cell dimensions	a = 14.7414(19) A alpha = 90 deg. b = 18.668(2) A beta = 90 deg. c = 13.5904(17) A gamma = 90 deg.
Volume, Z	3740.0(8) A^3, 4
Density (calculated)	1.568 Mg/m^3
Absorption coefficient	1.512 mm^-1
F(000)	1812
Crystal size	0.40 x 0.20 x 0.20 mm
Theta range for data collection	1.85 to 29.10 deg.
Limiting indices	-19<=h<=19, -25<=k<=18, -17<=l<=13
Reflections collected	22287
Independent reflections	4794 [R(int) = 0.0183]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4794 / 2 / 297
Goodness-of-fit on F^2	1.137
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.0899
R indices (all data)	R1 = 0.0449, wR2 = 0.0926
Largest diff. peak and hole	1.072 and -0.757 e.A^-3

NMR Characterization of 1.(400MHz, $CDCl_3$)
A1:^{1}H / B1:Cosy / C1: HMQC

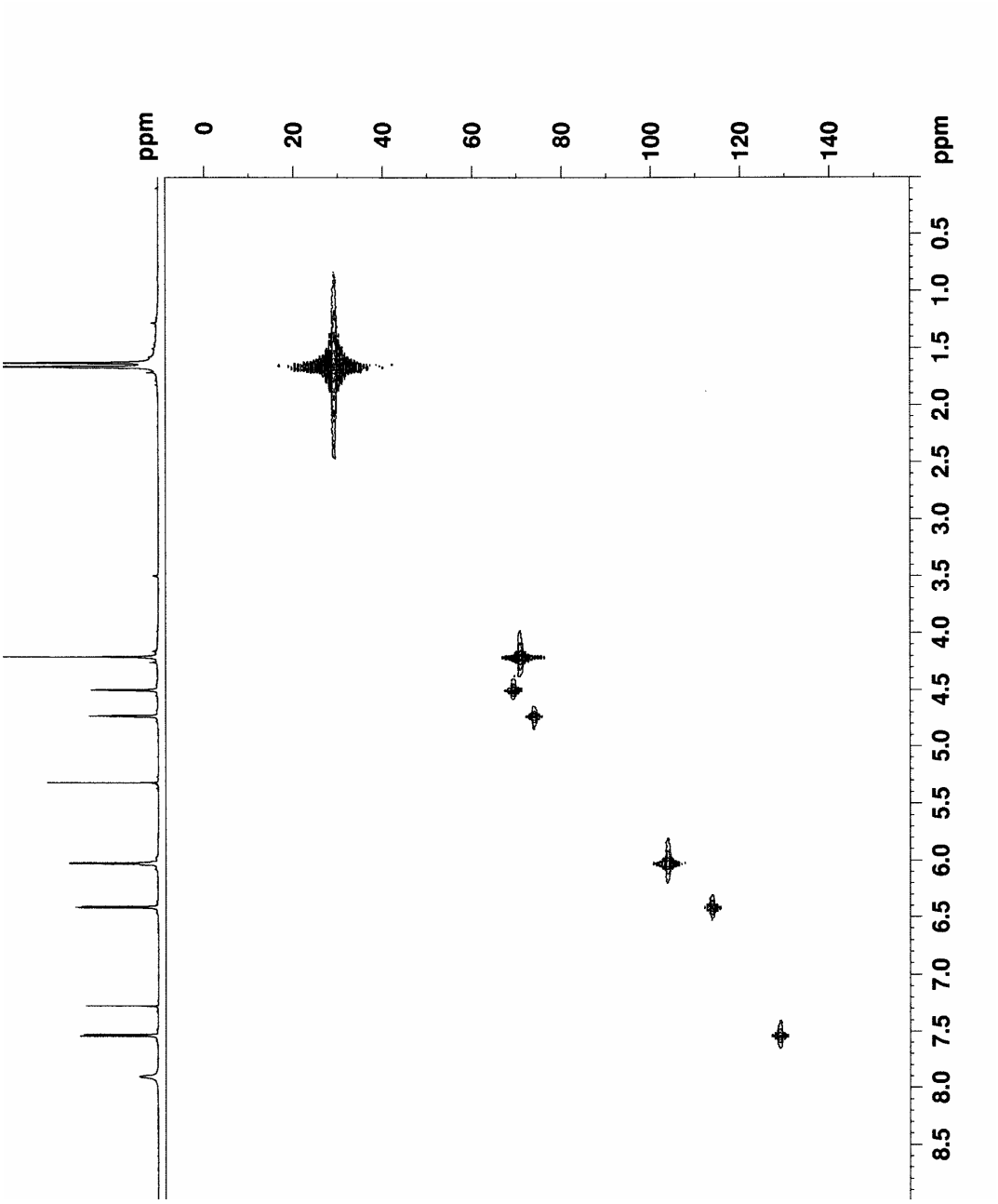
(A1) ^{1}H spectrum of **1** ($CDCl_3$, 400 MHz).



(B1) ^{1}H-^{1}H COSY map of **1** ($CDCl_3$, 400 MHz)

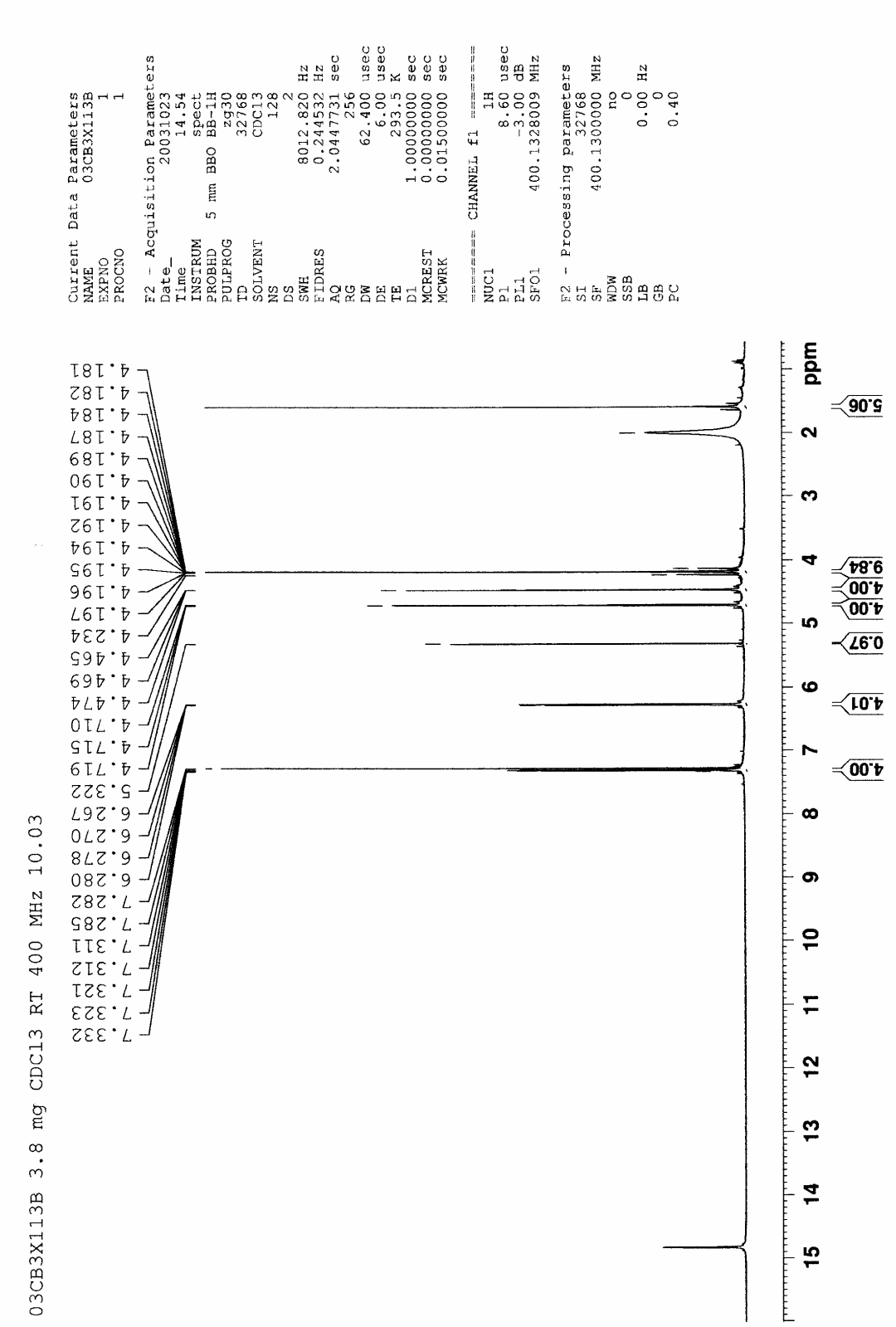


(C1) HMQC map of **1**($CDCl_3$, 400MHz)

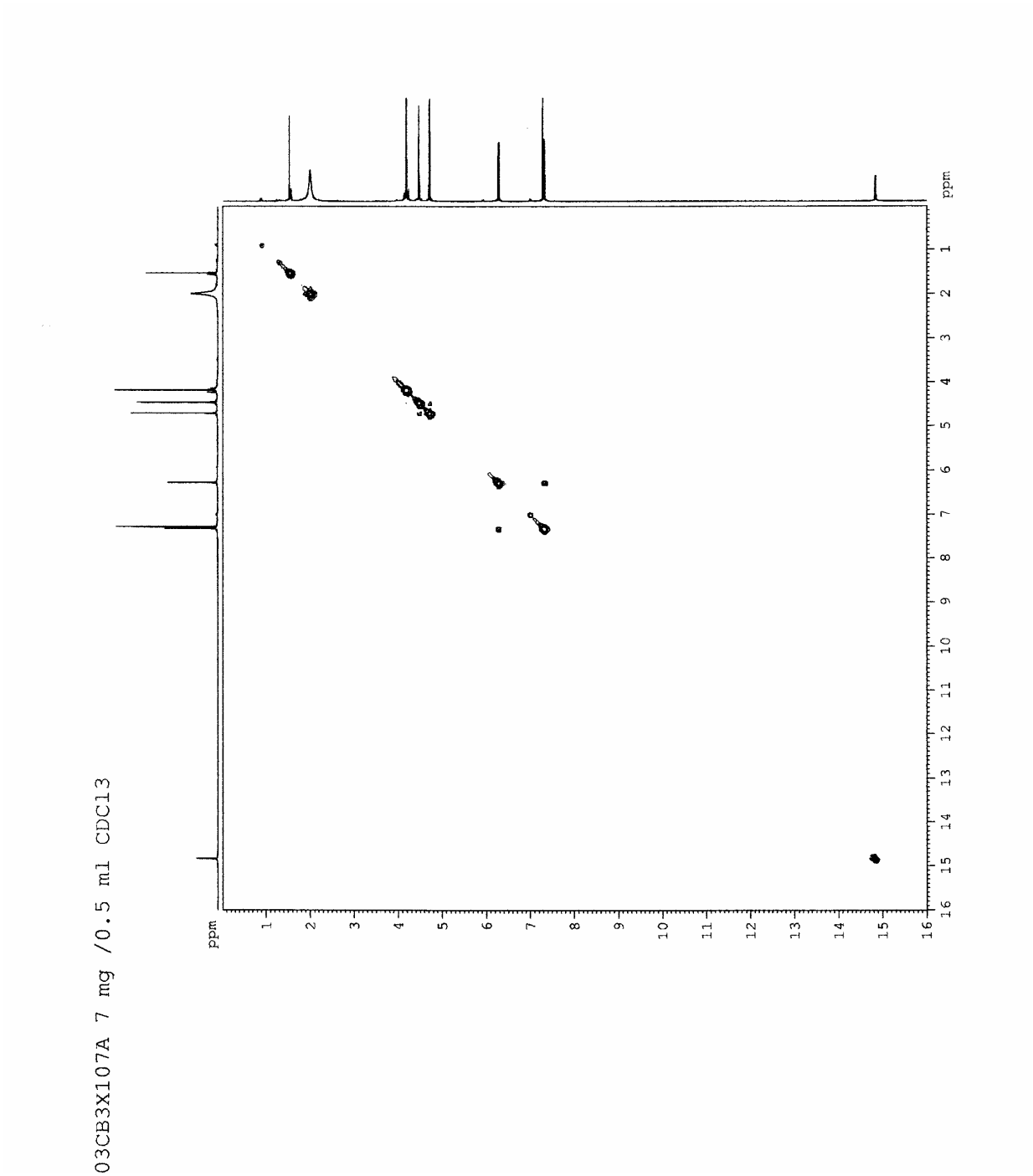


NMR Characterization of 2.(400MHz, $CDCl_3$)
A2:^{1}H / B2:Cosy / C2: HMQC

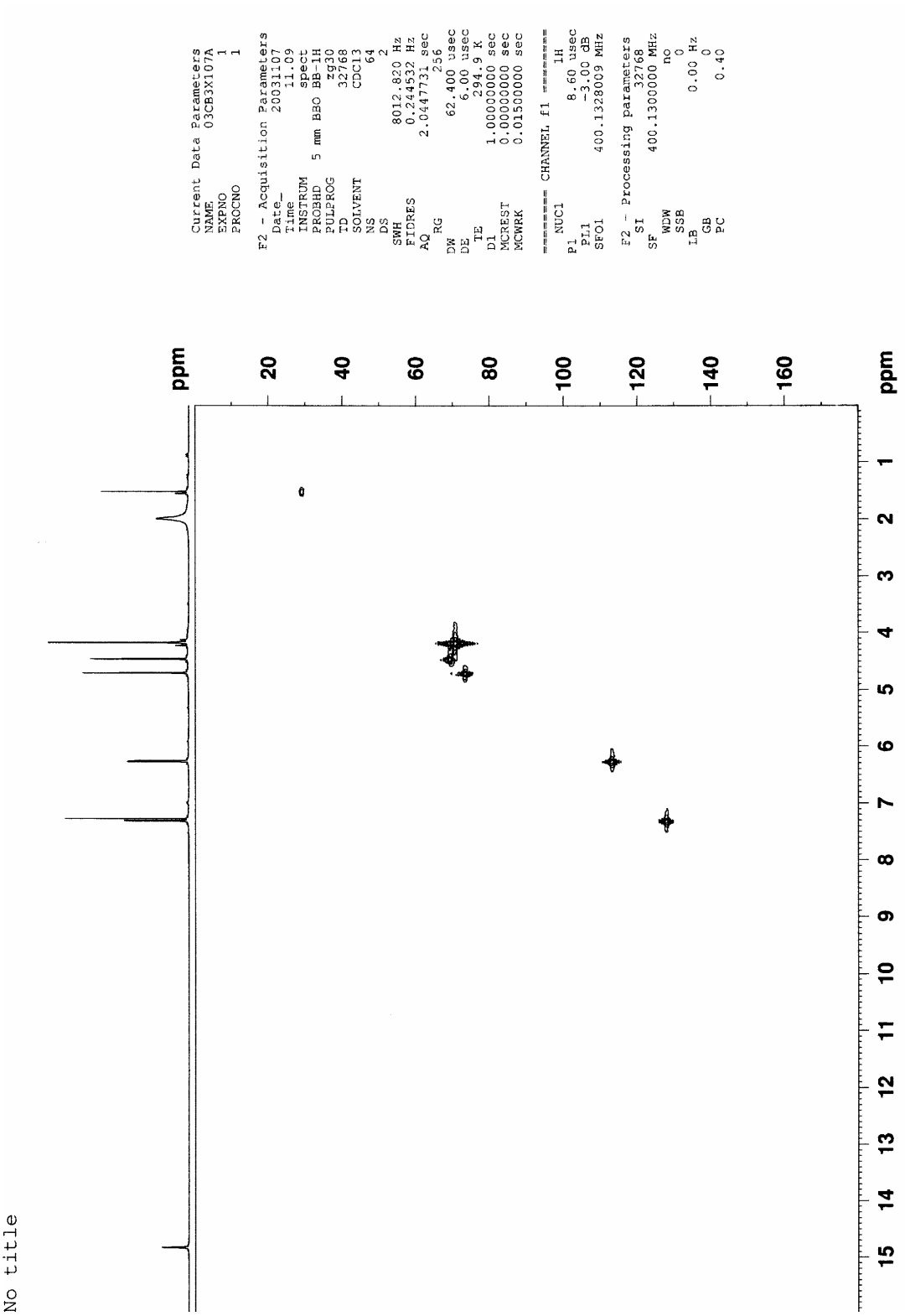
(A2) ^{1}H spectrum of **2** ($CDCl_3$, 400 MHz).



(B2) ^{1}H-^{1}H COSY map of **2** ($CDCl_3$, 400 MHz)

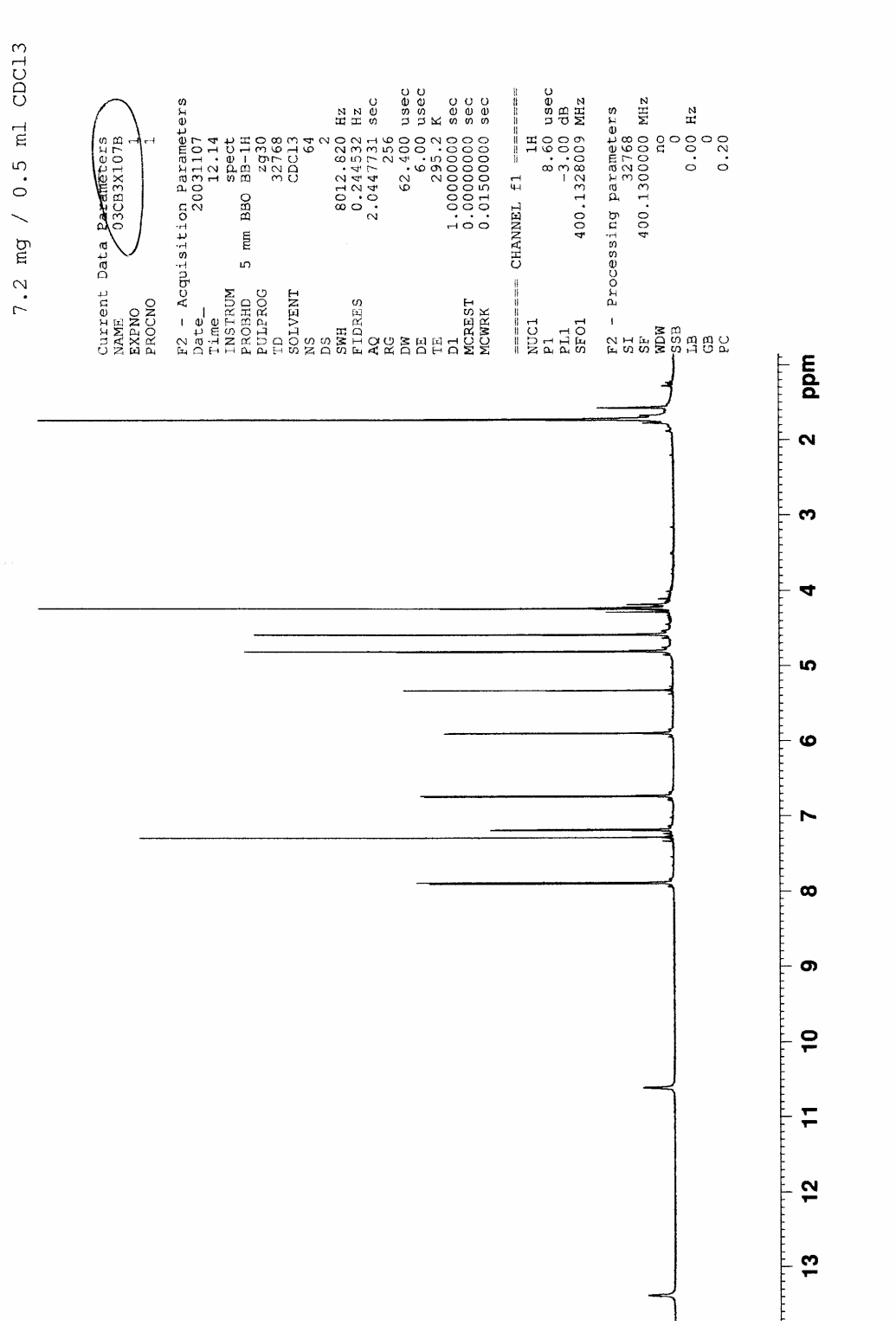


(C2) HMQC map of **2**($CDCl_3$, 400MHz)

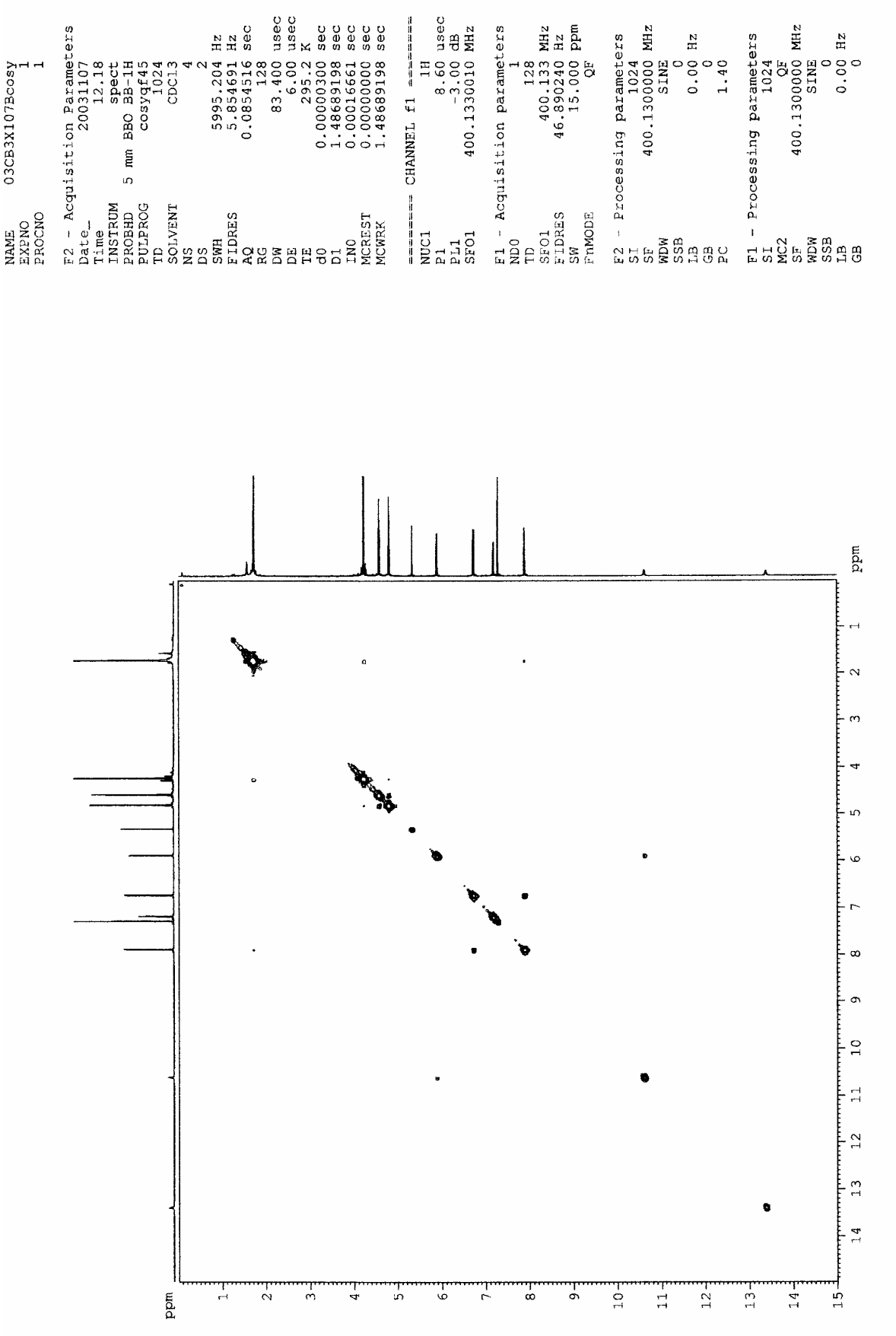


NMR Characterization of 3.(400MHz, $CDCl_3$)
A3:^{1}H / B32:Cosy / C3: HMQC

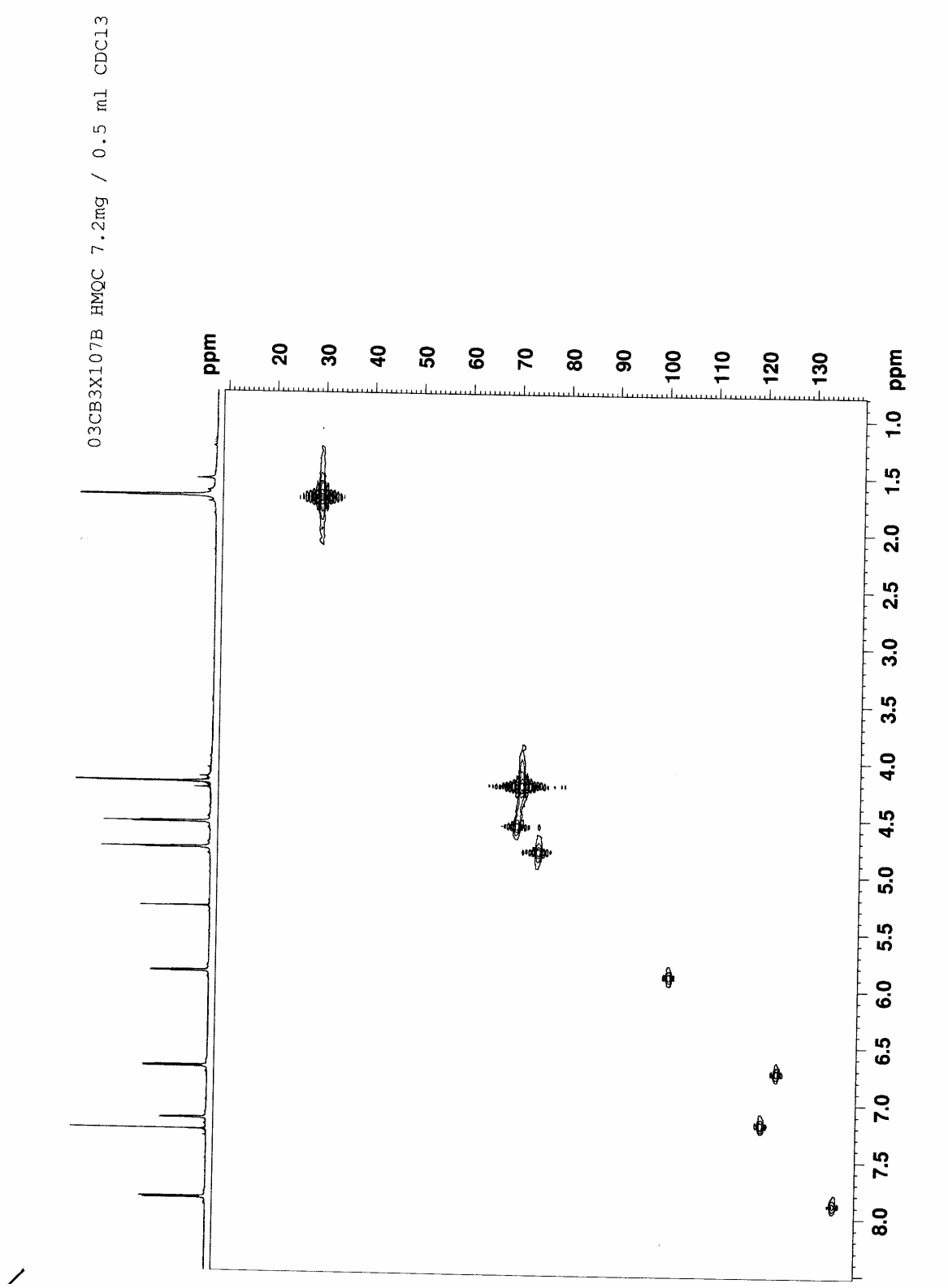
(A3) ^{1}H spectrum of **3** ($CDCl_3$, 400 MHz).



(B3) ^{1}H-^{1}H COSY map of **3** ($CDCl_3$, 400 MHz)

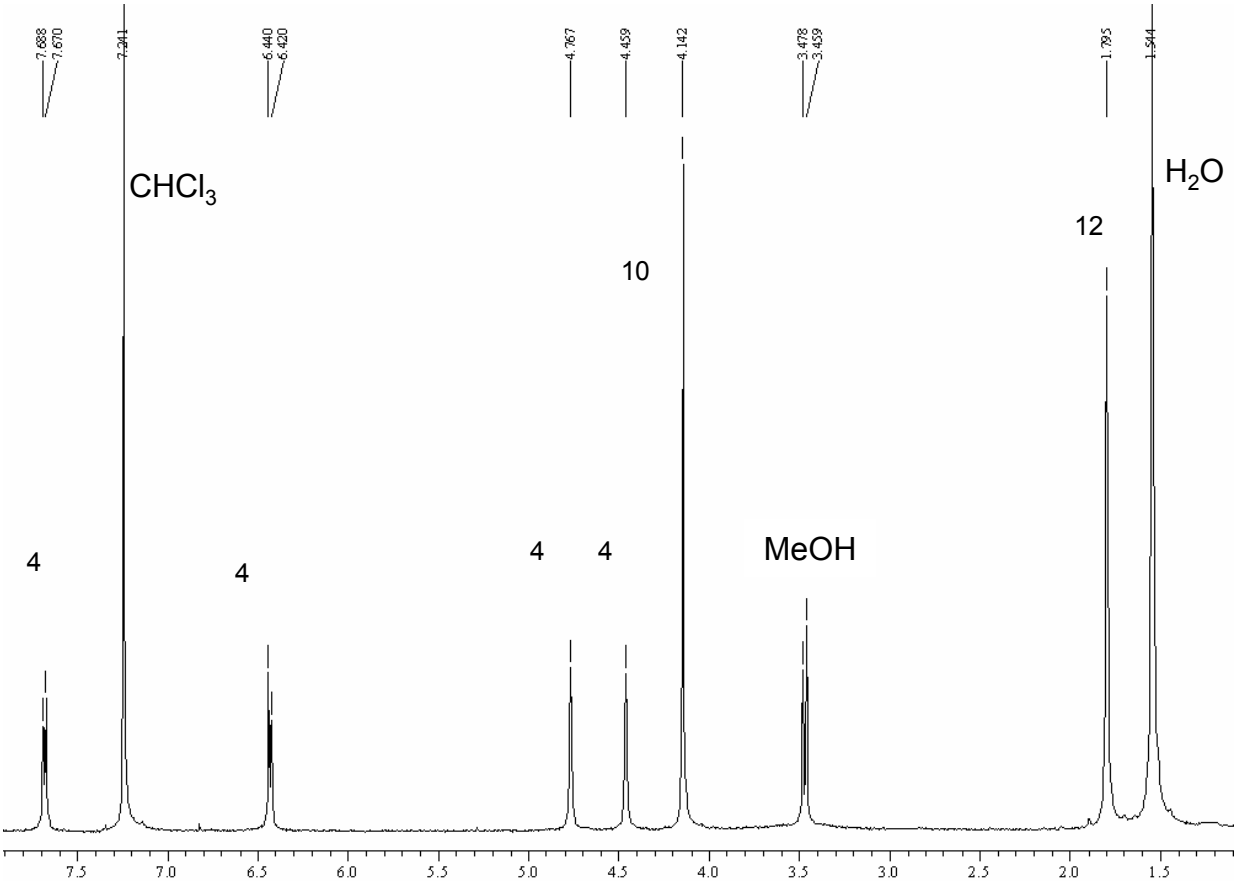


(C3) HMQC map of **3** ($CDCl_3$, 400MHz)

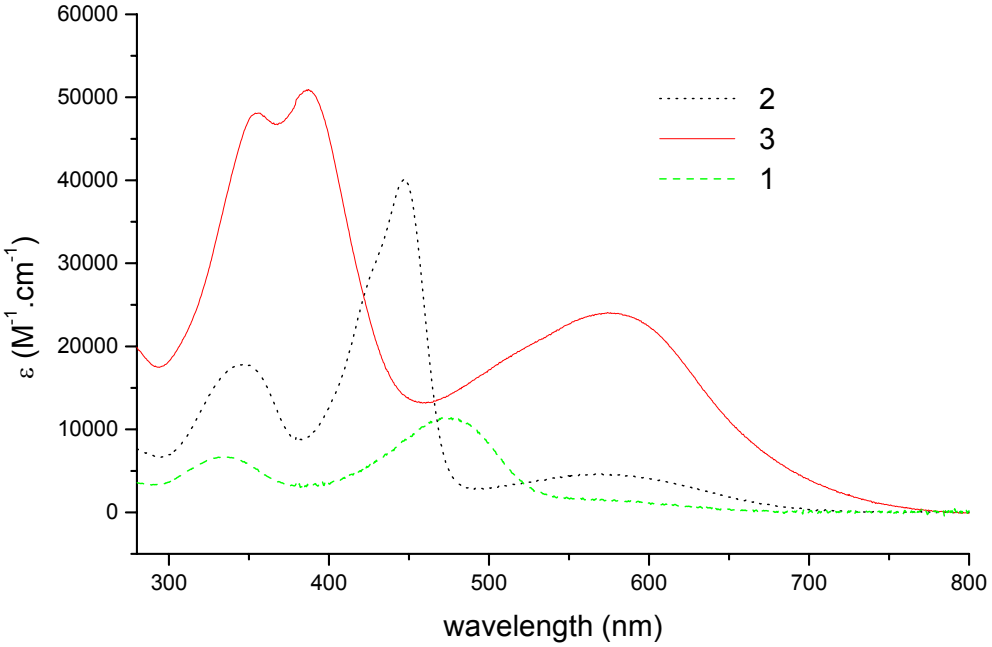


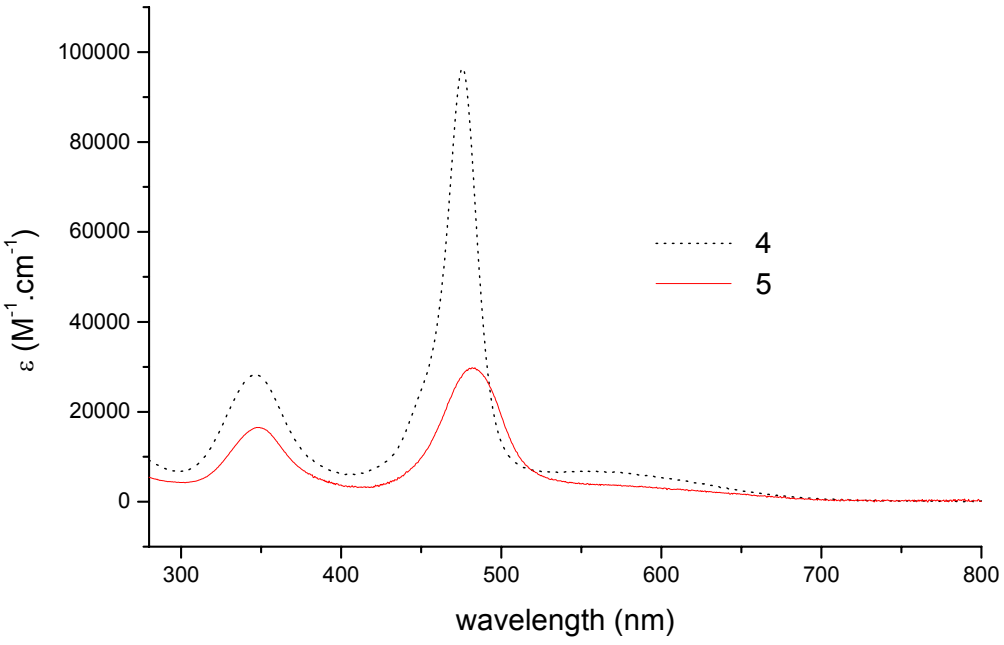
NMR Characterization of 4

^{1}H NMR spectrum of **4** ($CDCl_3$, 250 mHz)

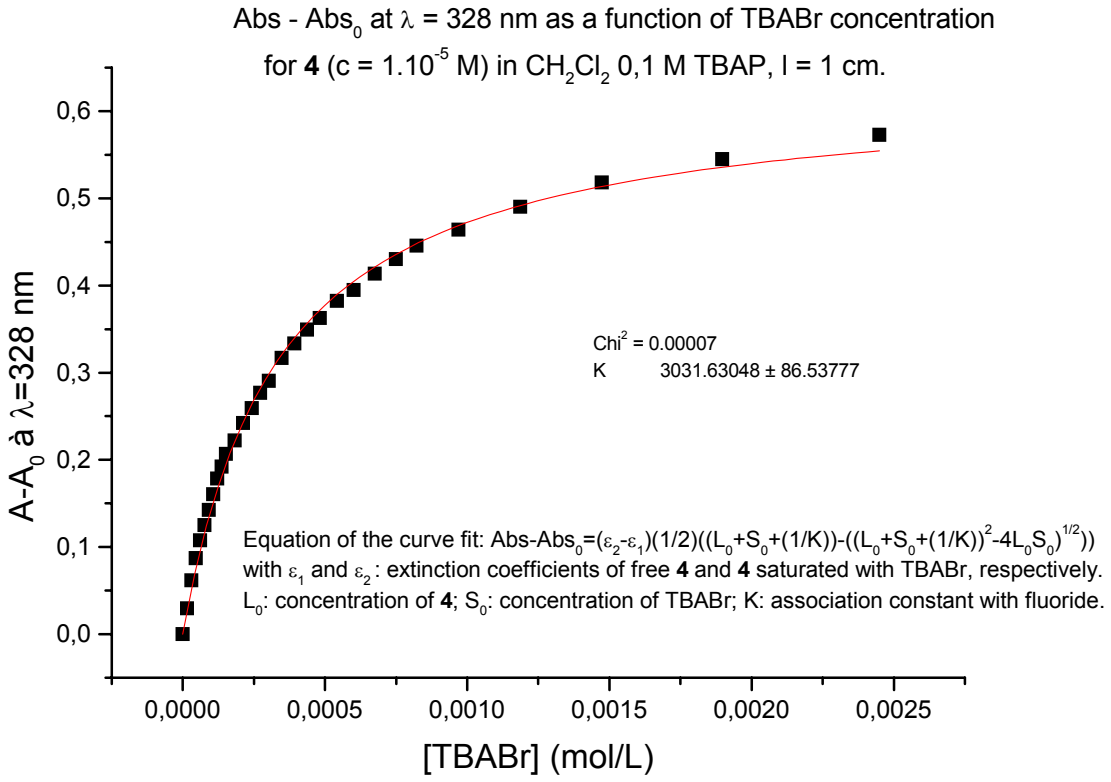


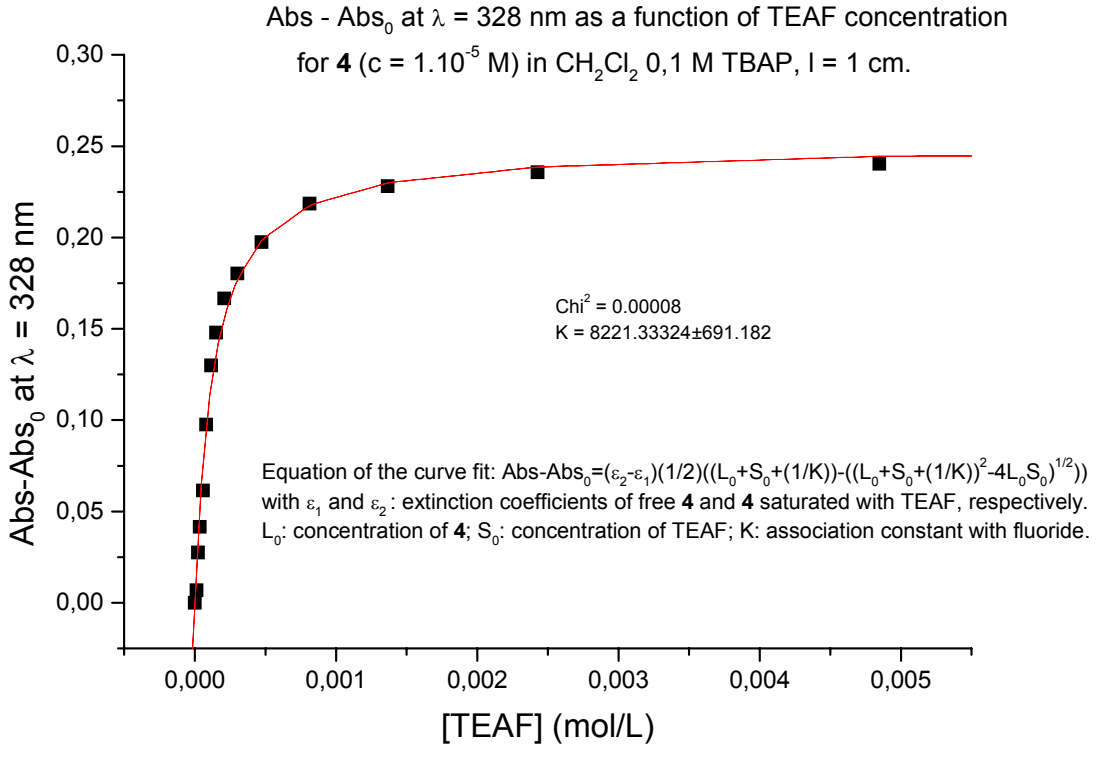
UV-Visible features recorded in dichloromethane at 20°C, C = 10^{-5} M, using a 1 cm cell.



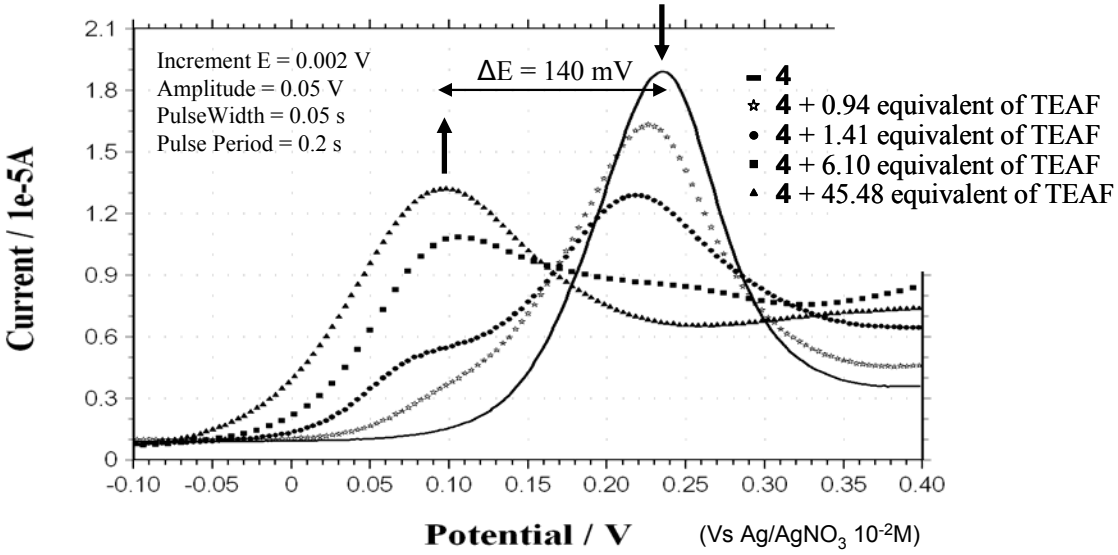


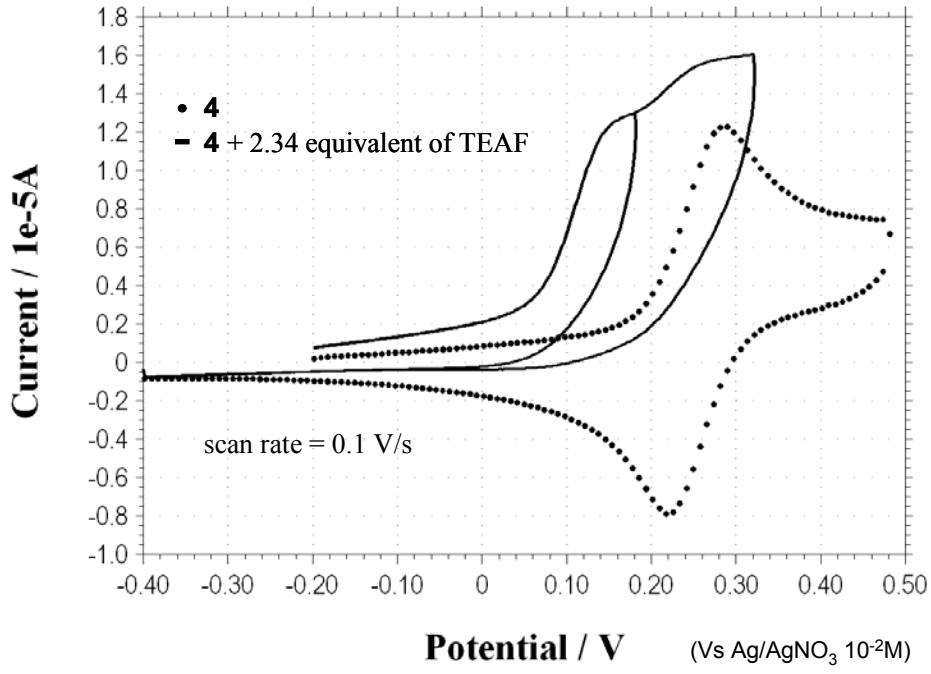
Spectrophotometric titration of 4 with Tetrabutylammonium bromide and Tetraethylammonium fluoride in CH_2Cl_2 (0.1M tetrabulylammonium perchlorate)





Evolution of the DPV and the CV curves recorded in a CH_2Cl_2 0,1 M TBAP solution of 4 (5×10^{-4} M) upon adding increasing amounts of tetraethylammonium fluoride (TEAF).
WE: vitreous carbon ø = 3 mm, Aux: Pt wire, Ref: $Ag/AgNO_3$ 10^{-2} M.





After the addition of 2.34 equivalent of TEAF the waves corresponding to the oxydation of the ferrocene in the free complexe and with the fluoride become both irrversible.