Synthesis and Conformational Studies on Hexa-*O*-Alkyl *p*-Unsubstituted Calix[6]arenes

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Supporting Information

General Methods. Unless otherwise reported, all reactions were carried out under dry and deoxygenated argon atmosphere. Solvents were freshly distilled and dried before use by standard methods. All chemicals were used as purchased. Reported melting points are uncorrected and were measured in open capillaries on a Gallenkamp Melting Point apparatus. The NMR experiments (^{1}H, ^{13}C{^{1}H}, COSY (H,H), HMQC and ROESY) were carried out at 500 (125) MHz and reported chemical shifts (δ) are externally referenced to solvent residual signal and given in ppm. Mass spectra were performed on a REFLEX spectrometer by MALDI-TOF method, using ditranol as matrix and NaI as additive. Elemental analyses, performed on a LECO CHN 932 microanalyser and reported as percentage, indicated inclusion of solvent molecules for nearly all calixarene products and were supported by separate ^{1}H NMR studies. TLC was performed on silica gel Alugram Sil G/UV254 (Macherey-Nagel). Compounds **1**[1] and **4**[2] were synthesized according to described procedures.

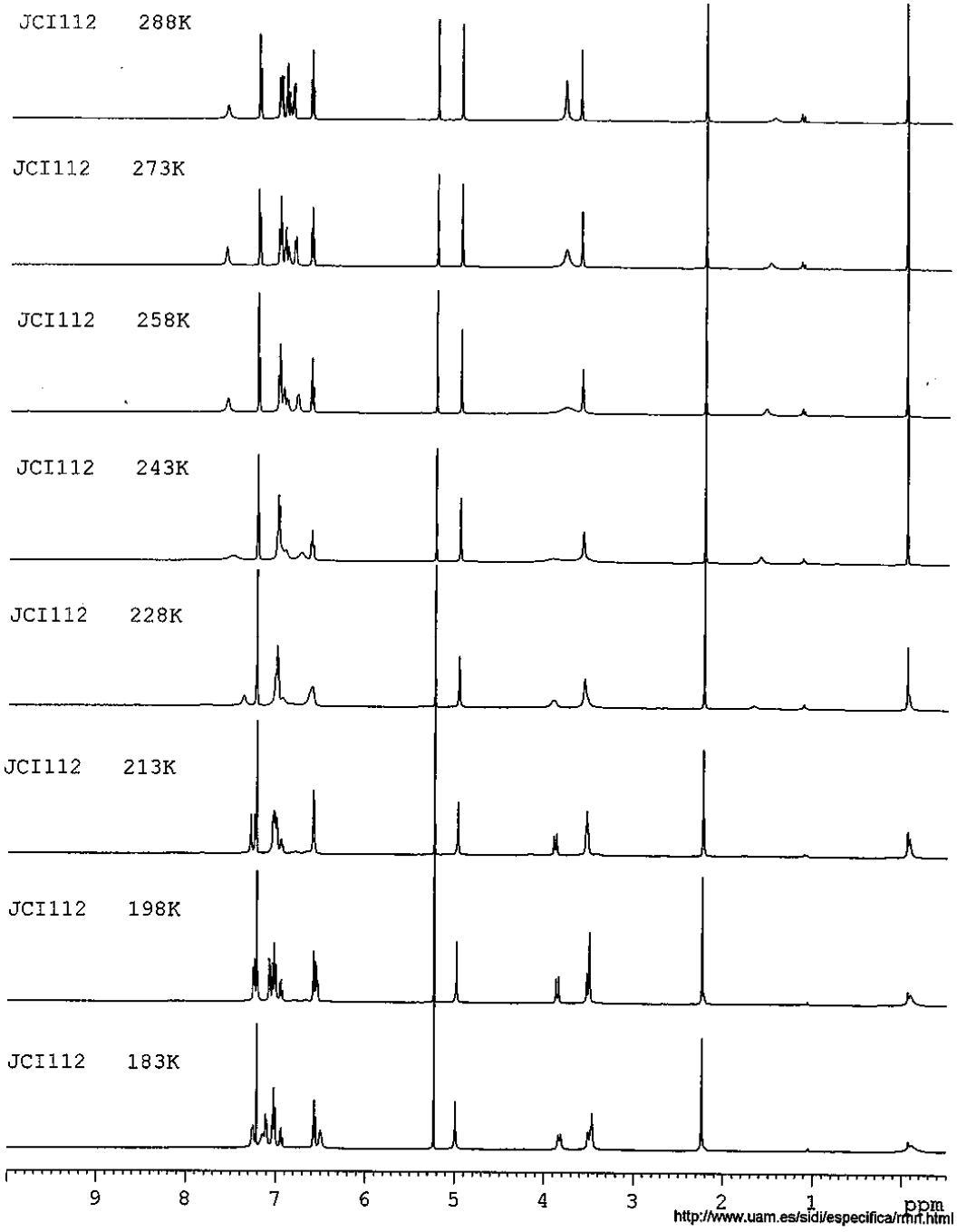
[1] Gutsche, C. D.; Lee-Gin, L. *Tetrahedron* **1986**, *42*, 1633-1640.

[2] Kanamathareddy, S.; Gutsche, C. D. *J. Org. Chem*. **1992**, *57*, 3160-3166.

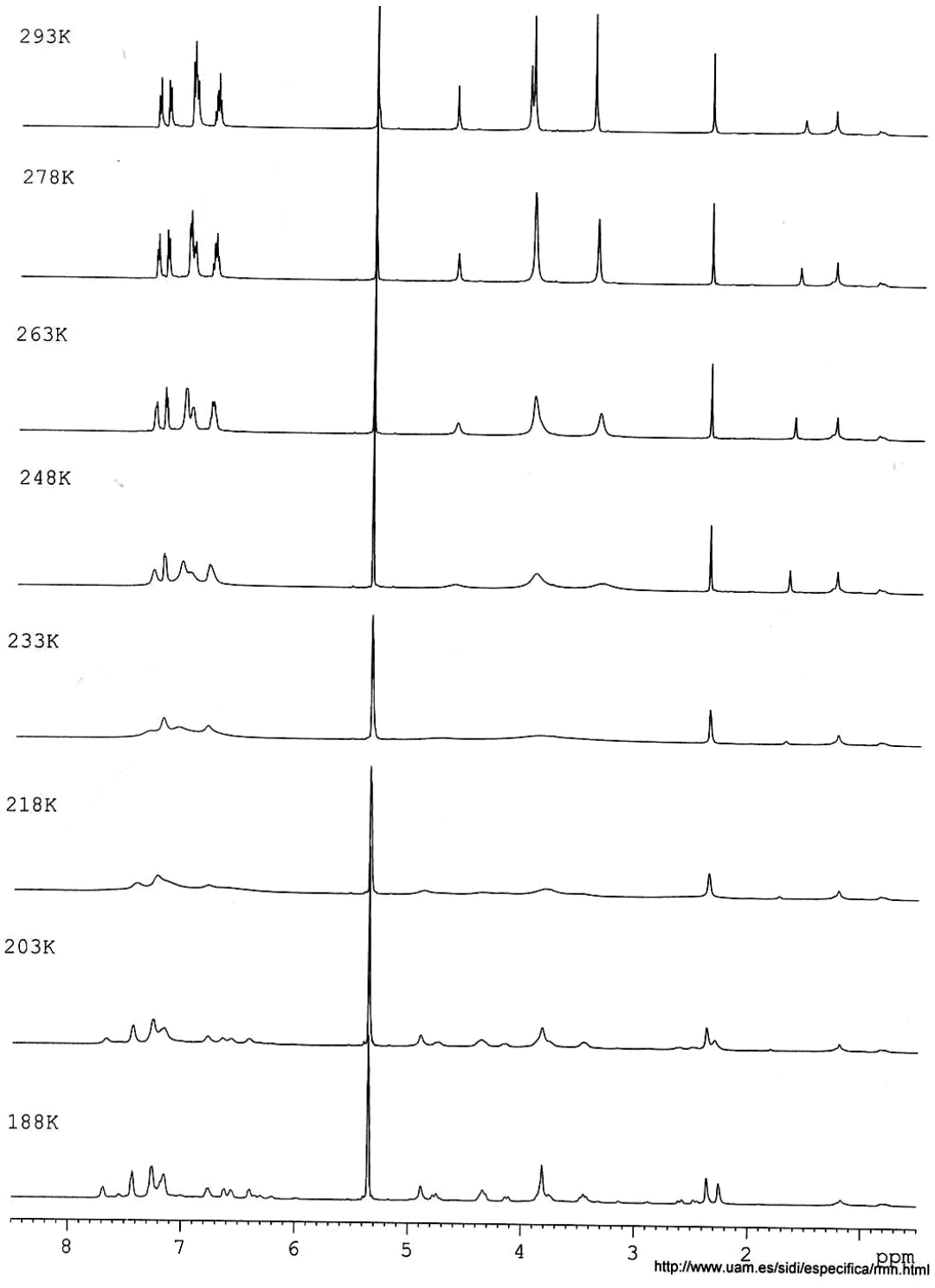
Table S1. Crystal data and structure refinement for compounds **3a**, **3b**, and **3d**.

	3a	**3b•CH_2Cl_2**	**3d**
Empirical formula	$C_{70}H_{68}O_{14}$	$C_{83}H_{94}Cl_2O_{14}$	$C_{80}H_{86}Br_2O_{14}$
Formula weight	1133.24	1384.47	1431.31
Temperature (K)	296(2)	100(2)	297(2)
Wavelength (Å)	1.54178	1.54178	1.54178
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c	P2(1)/c
a (Å)	12.0726(7)	11.17490(10)	11.8114(2)
b (Å)	22.2121(11)	12.11860(10)	21.0977(4)
c (Å)	12.0726(7)	27.6517(3)	15.8270(3)
α, β, γ (º)	90, 113.741(2), 90	90, 90.6070(10), 90	90, 109.6400(10), 90
Volume ($Å^3$)	2963.4(3)	3744.50(6)	3714.53(12)
Z	2	2	2
Density (calculated) (mg/m^3)	1.270	1.228	1.280
Absorption coefficient (mm^{-1})	0.715	1.296	1.890
F(000)	1200	1472	1496
Crystal size (mm)	0.08 × 0.05 × 0.04	0.24 × 0.22 × 0.20	0.08 × 0.04 × 0.04
θ range for data collection (º)	3.98 to 66.99	3.20 to 70.65	3.63 to 70.55
Index ranges (*h*,*k*,*l*)	-14:13, -21:26, -12:13	-11:13, -14:14, -30:32	-14:13, -23:24, -18:19
Reflections collected	14814	23513	23758
Independent reflections	4866 [R(int) = 0.0612]	6892 [R(int) = 0.0264]	6808 [R(int) = 0.0418]
Completeness to θ (%)	66.99º, 91.8	70.65º, 95.8	70.55º, 95.6
Absorption correction	Semi-empirical from equivalents		SADABS v. 2.03
Max. and min. transmission	0.972 and 0.958	0.772 and 0.769	
Refinement method	Full-matrix least-sq. on F^2		
Data/restraints/parameters	4866/0/382	6892/0/635	6808/0/436
Goodness-of-fit on F^2	1.033	1.046	1.049
Final R / *w*R2 [I>2sigma(I)]	0.0619, 0.1701	0.0467, 0.1149	0.0880, 0.2567
R / *w*R2 (all data)	0.0850, 0.1907	0.0521, 0.1192	0.1218, 0.2944
Min/max resd. dens. ($e/Å^3$)	0.264 and -0.207	0.937 and -0.896	1.054 and -0.714

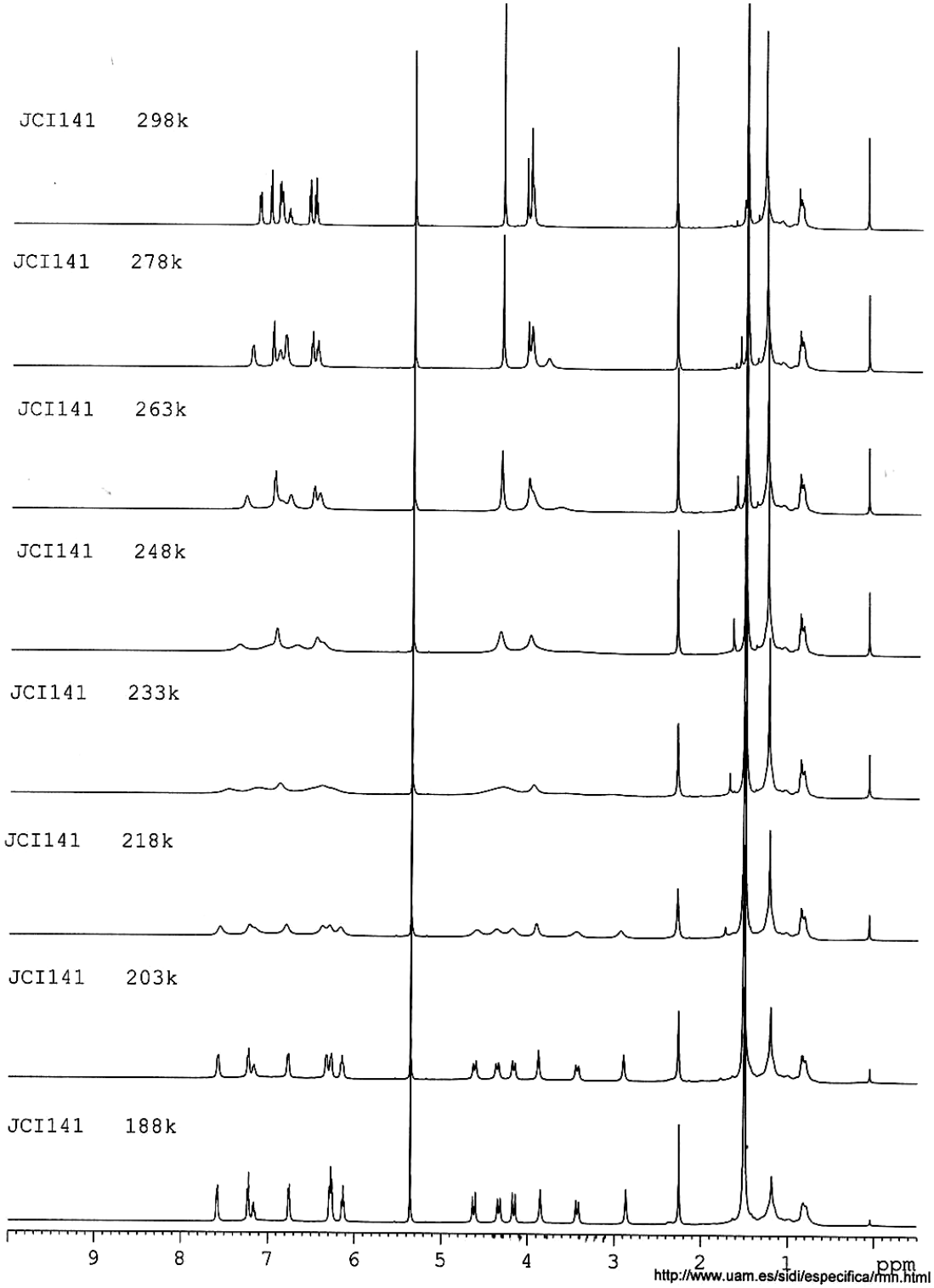
VT-^{1}H NMR spectra (288–188 K) of **2a** (CD_2Cl_2, 500 MHz)



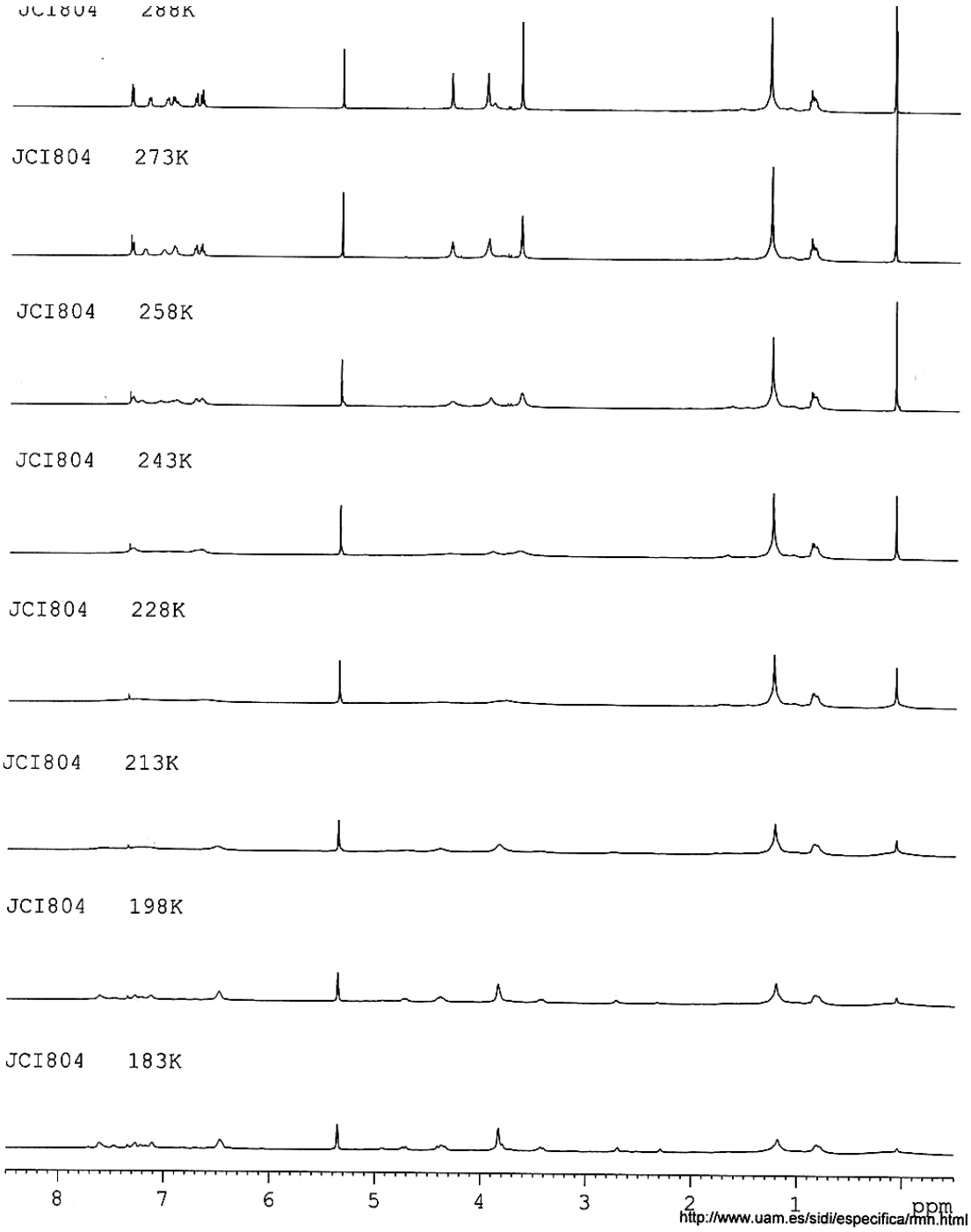
VT-^{1}H NMR spectra (293–188 K) of **3a** (CD_2Cl_2, 500 MHz)



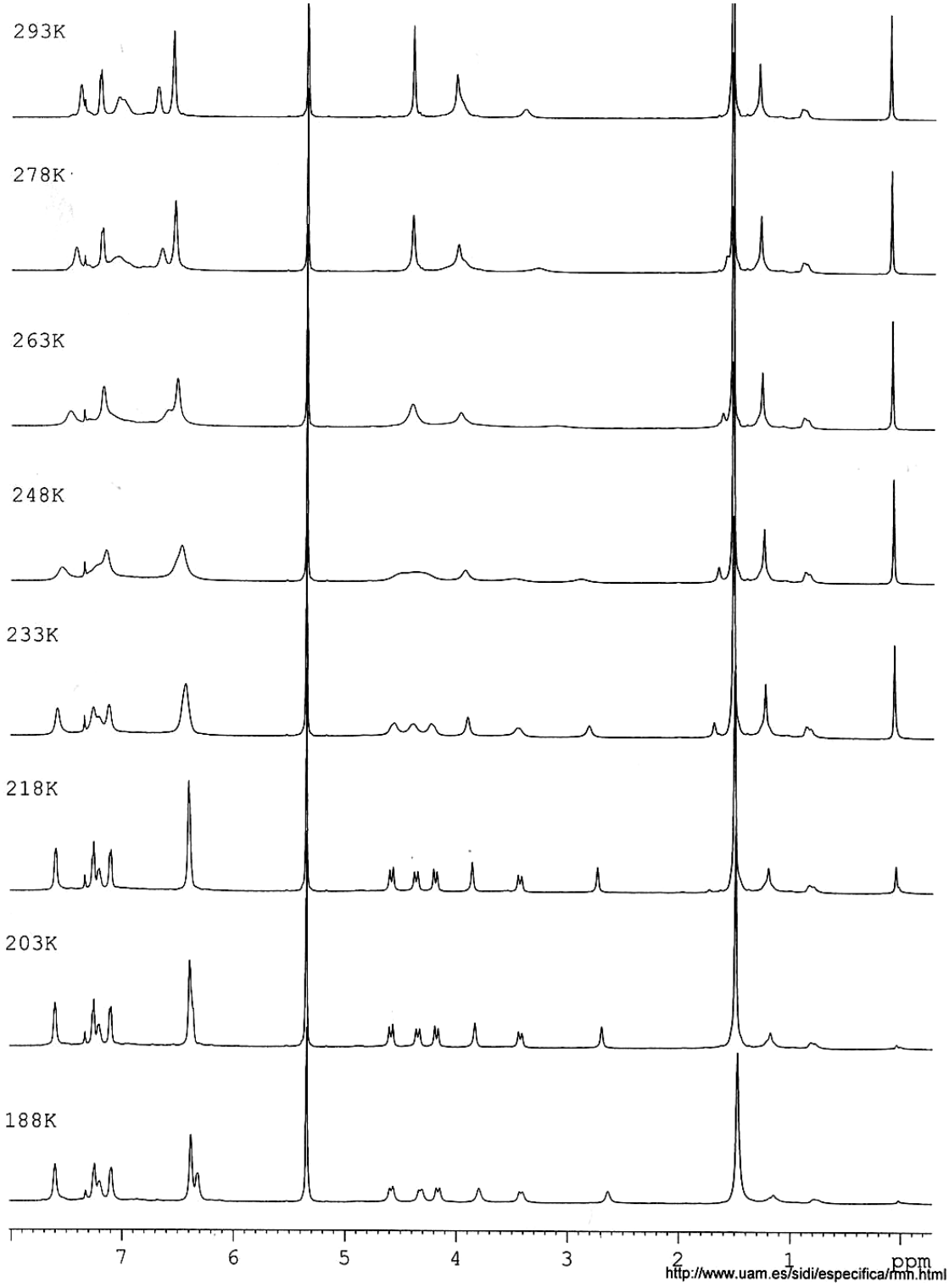
VT-^{1}H NMR spectra (298–188 K) of **3b** (CD_2Cl_2, 500 MHz)



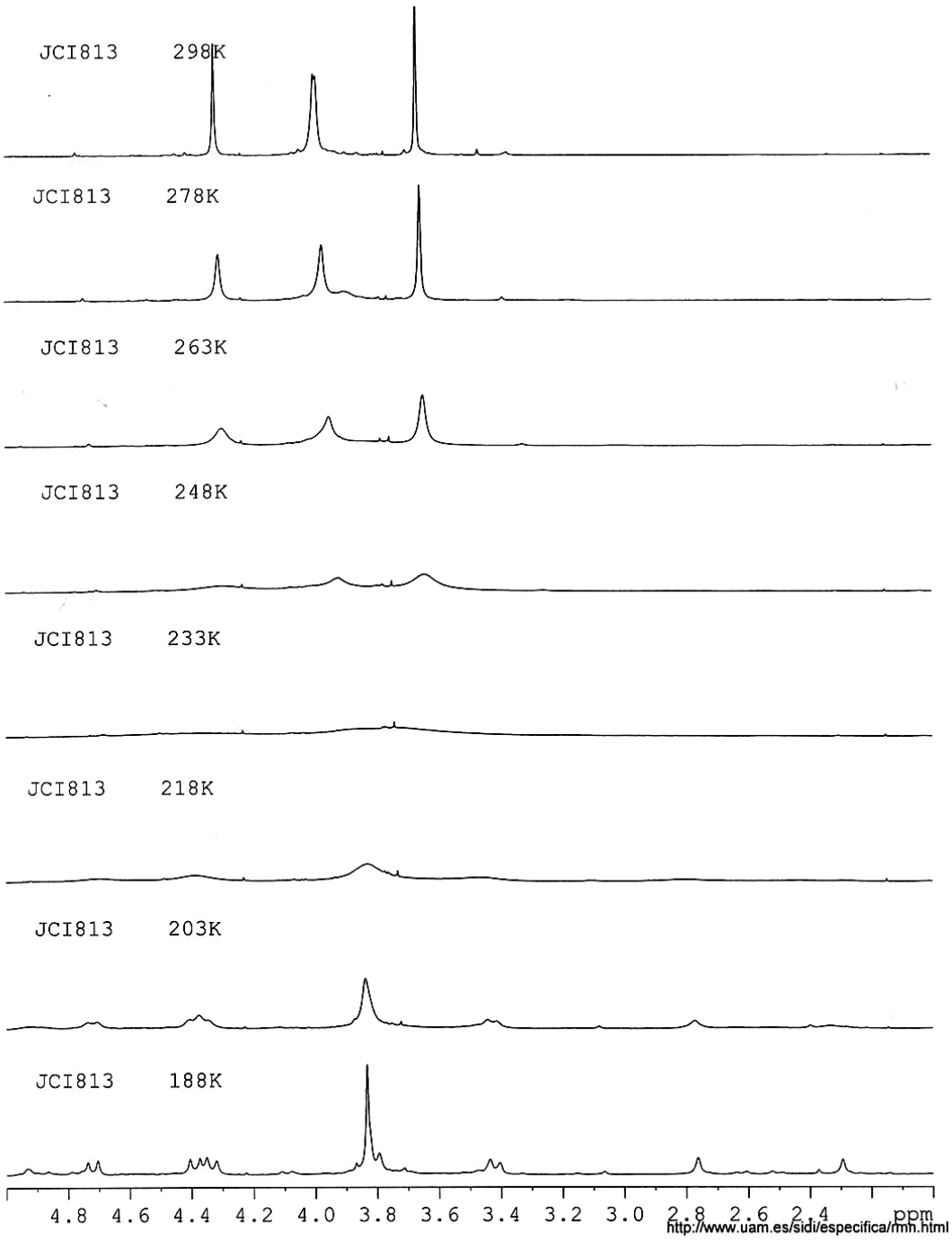
VT-^{1}H NMR spectra (288–188 K) of **3c** (CD_2Cl_2, 500 MHz)



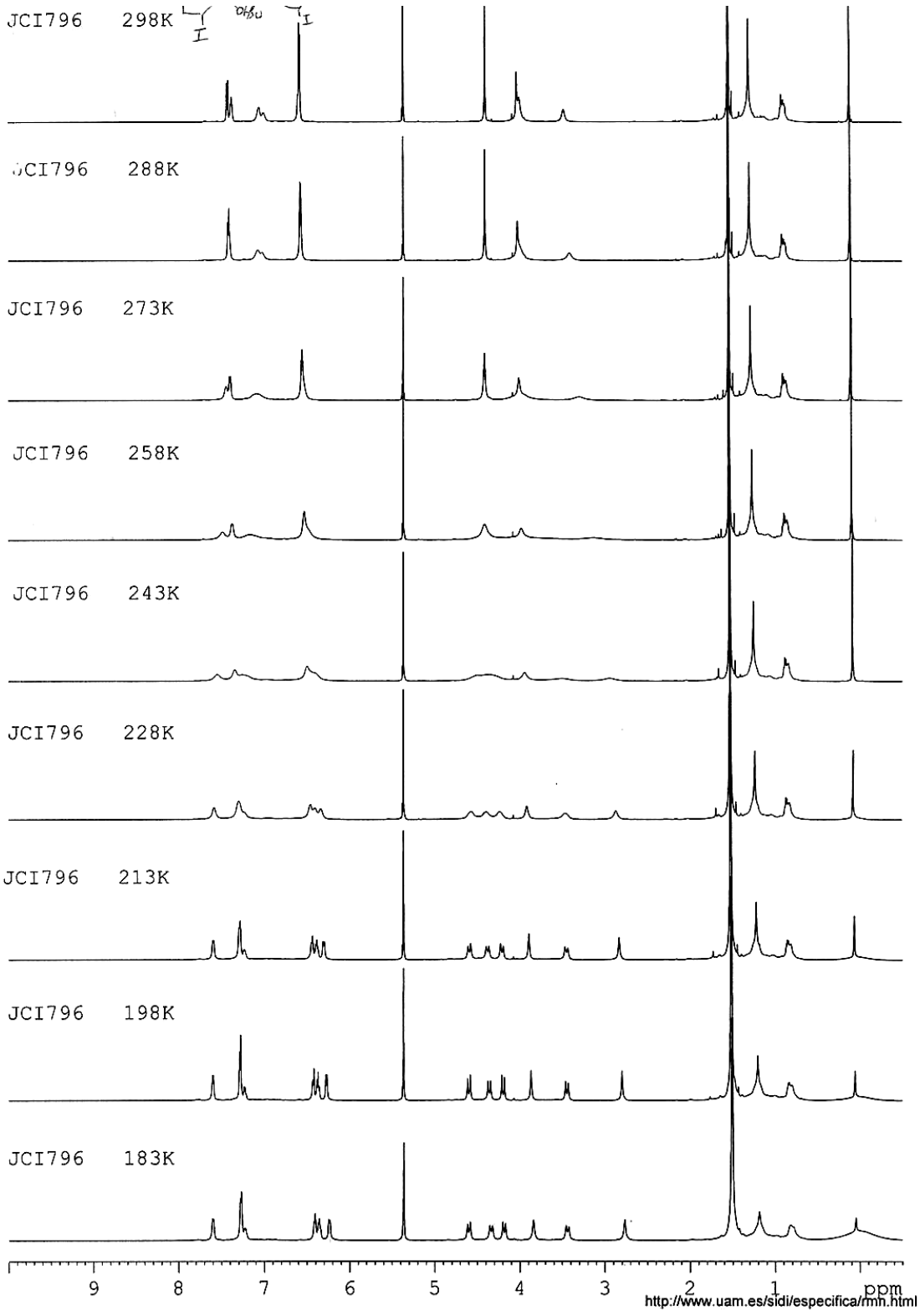
VT-^{1}H NMR spectra (293–188 K) of **3d** (CD_2Cl_2, 500 MHz)



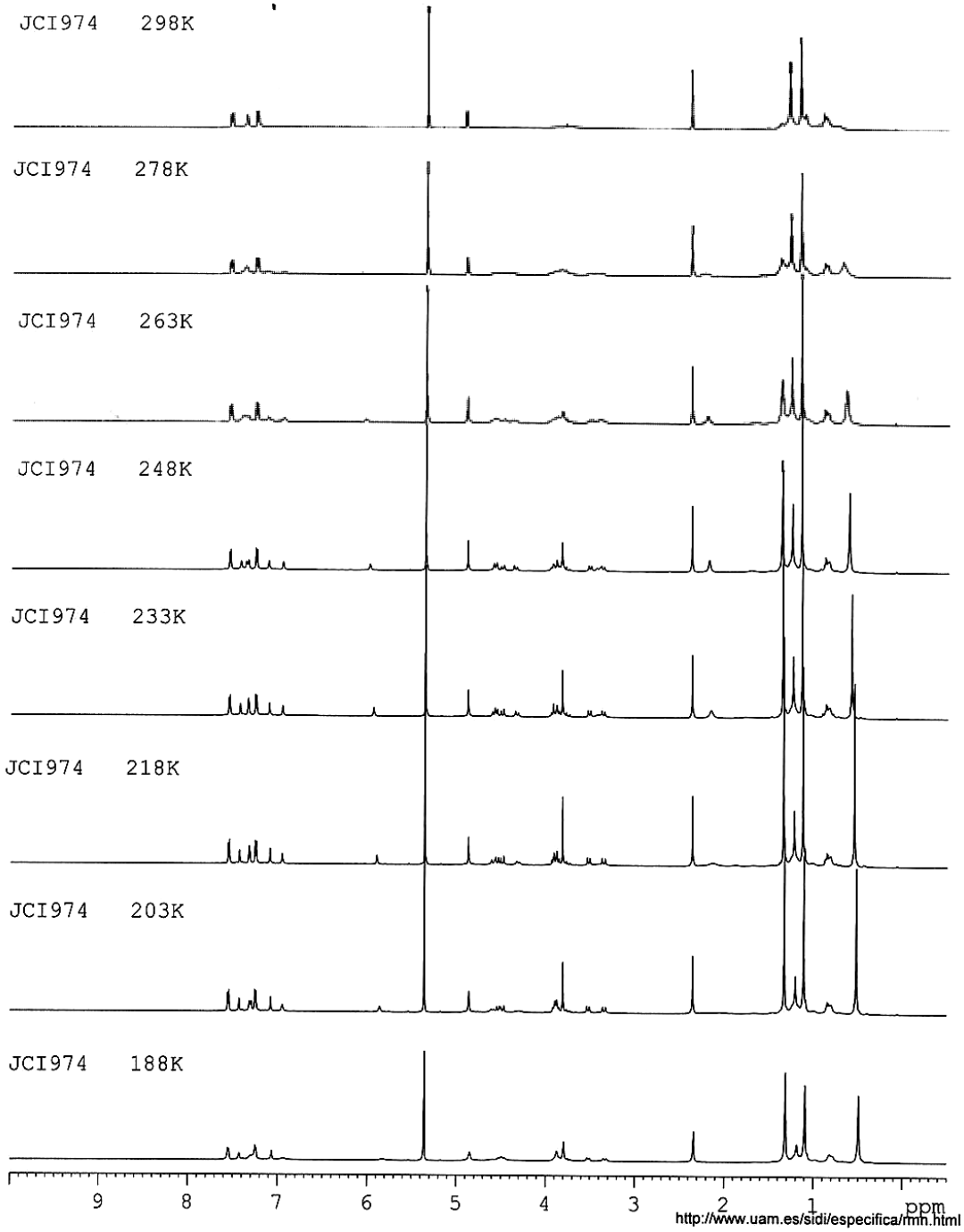
VT-^{1}H NMR spectra (298–188 K) of **3e** (CD_2Cl_2, 500 MHz)



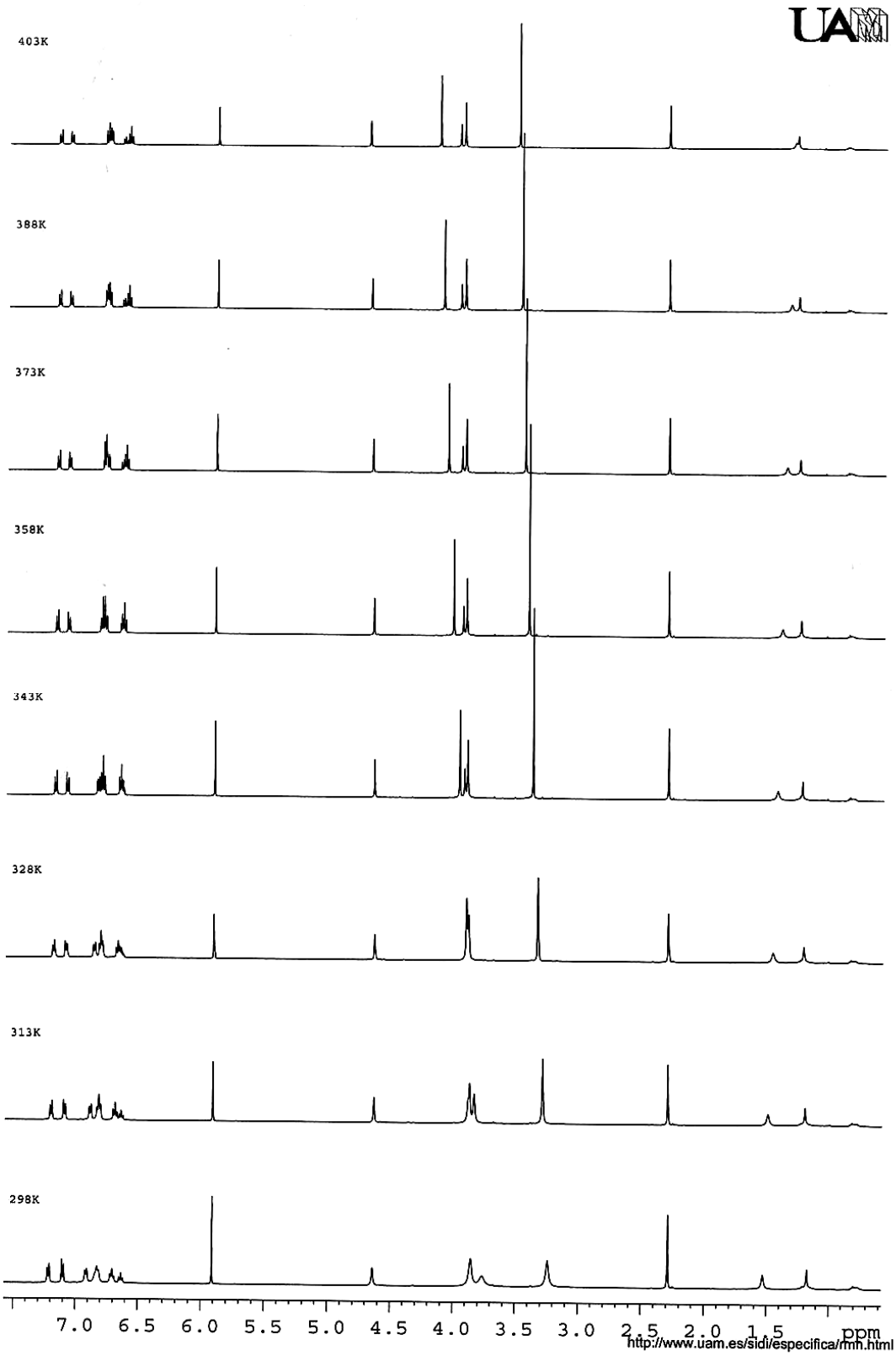
VT-^{1}H NMR spectra (298–188 K) of **3f** (CD_2Cl_2, 500 MHz)



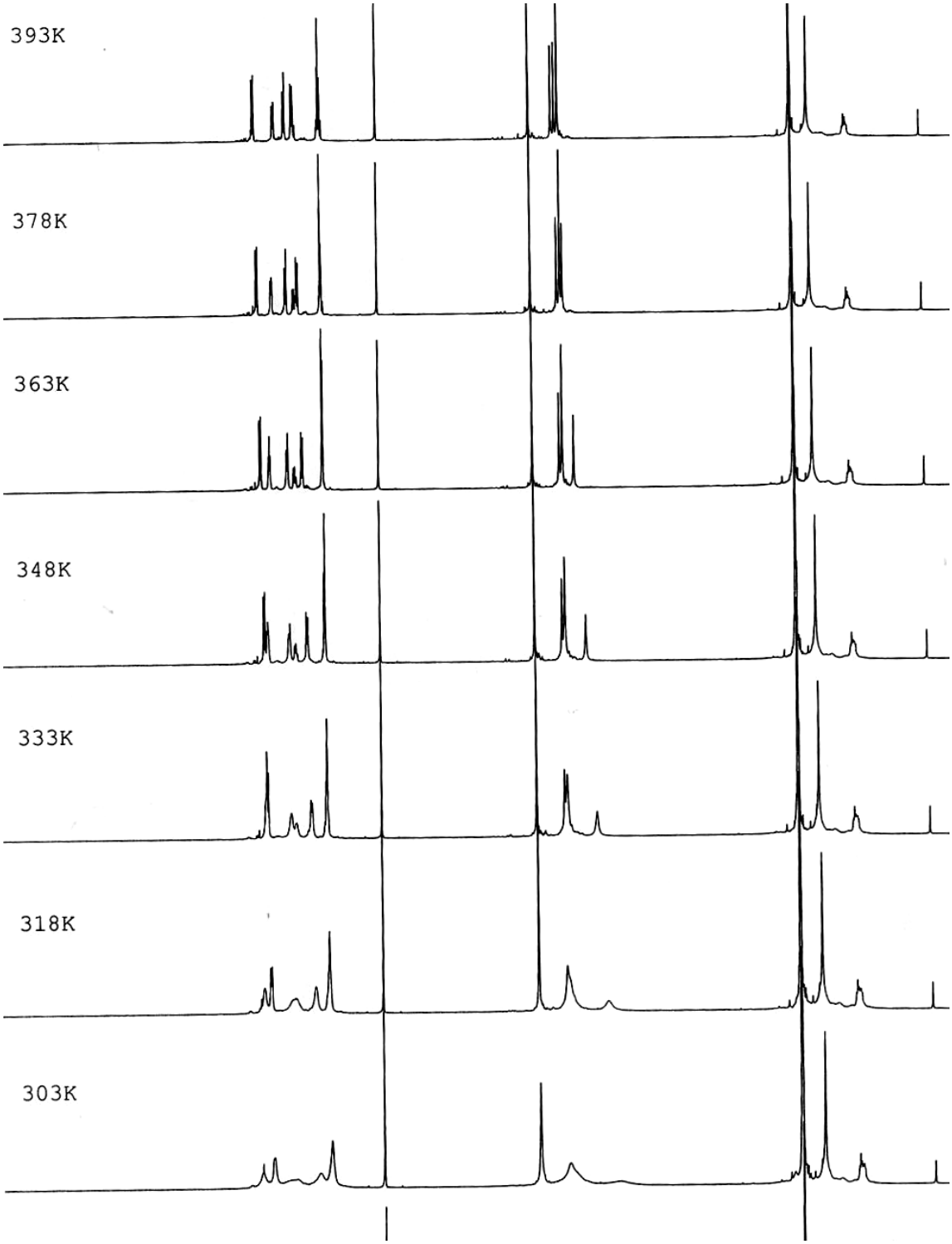
VT-^{1}H NMR spectra (298–188 K) of **5a** (CD_2Cl_2, 500 MHz)



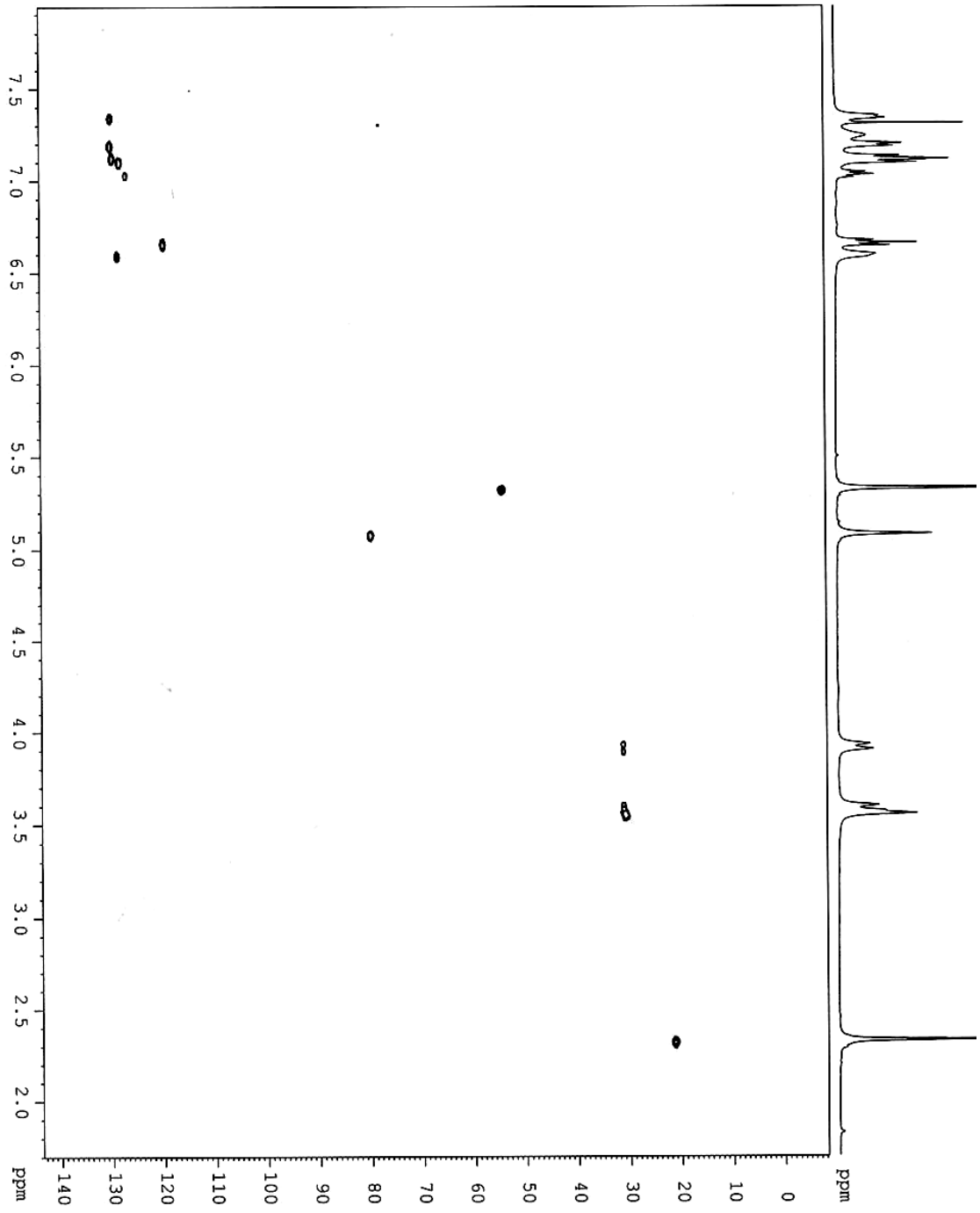
VT-^{1}H NMR spectra (403–298 K) of **3a** ($C_2D_2Cl_4$, 500 MHz)



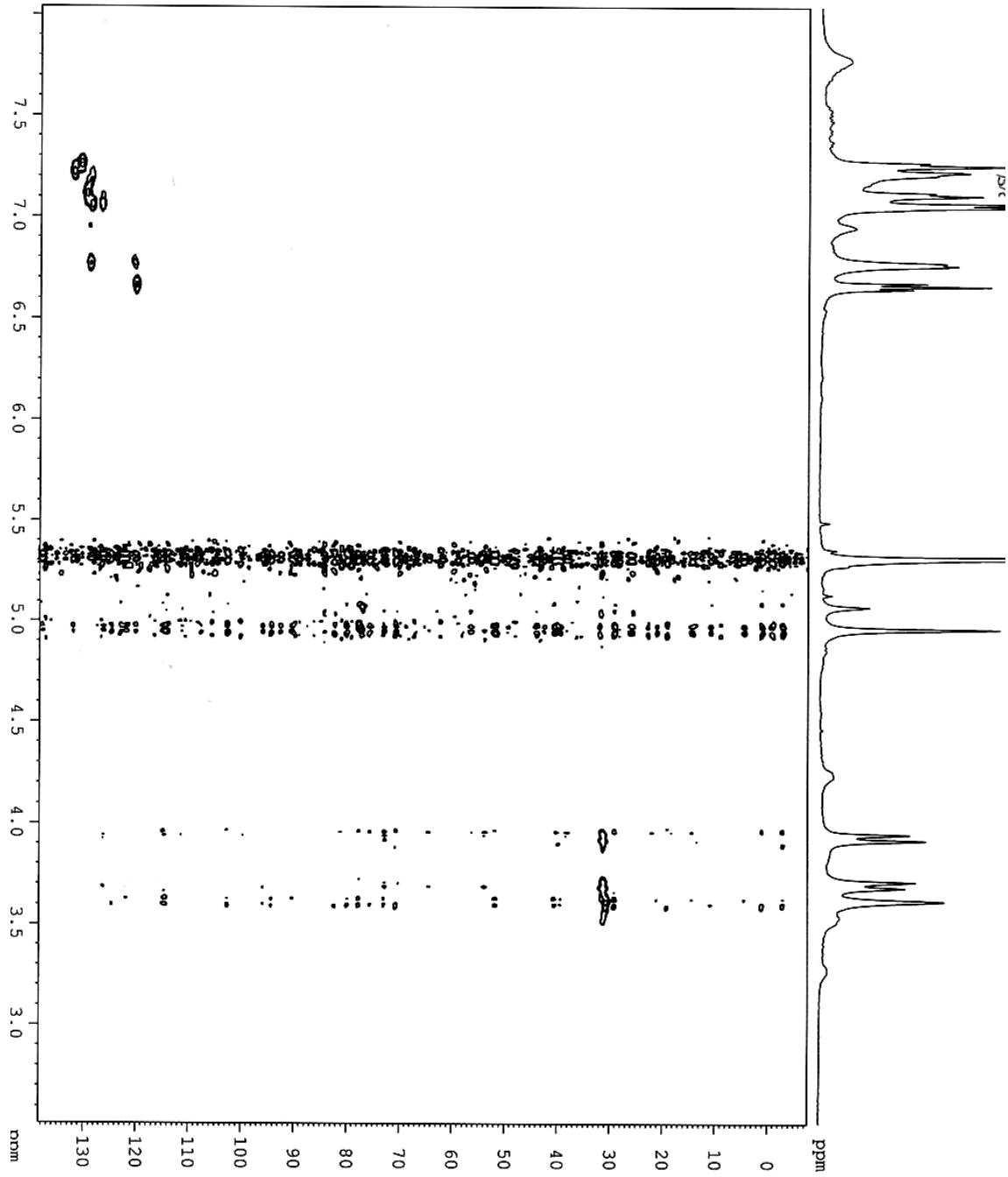
VT- ^{1}H NMR spectra (403–298 K) of **3d** ($C_2D_2Cl_4$, 500 MHz)



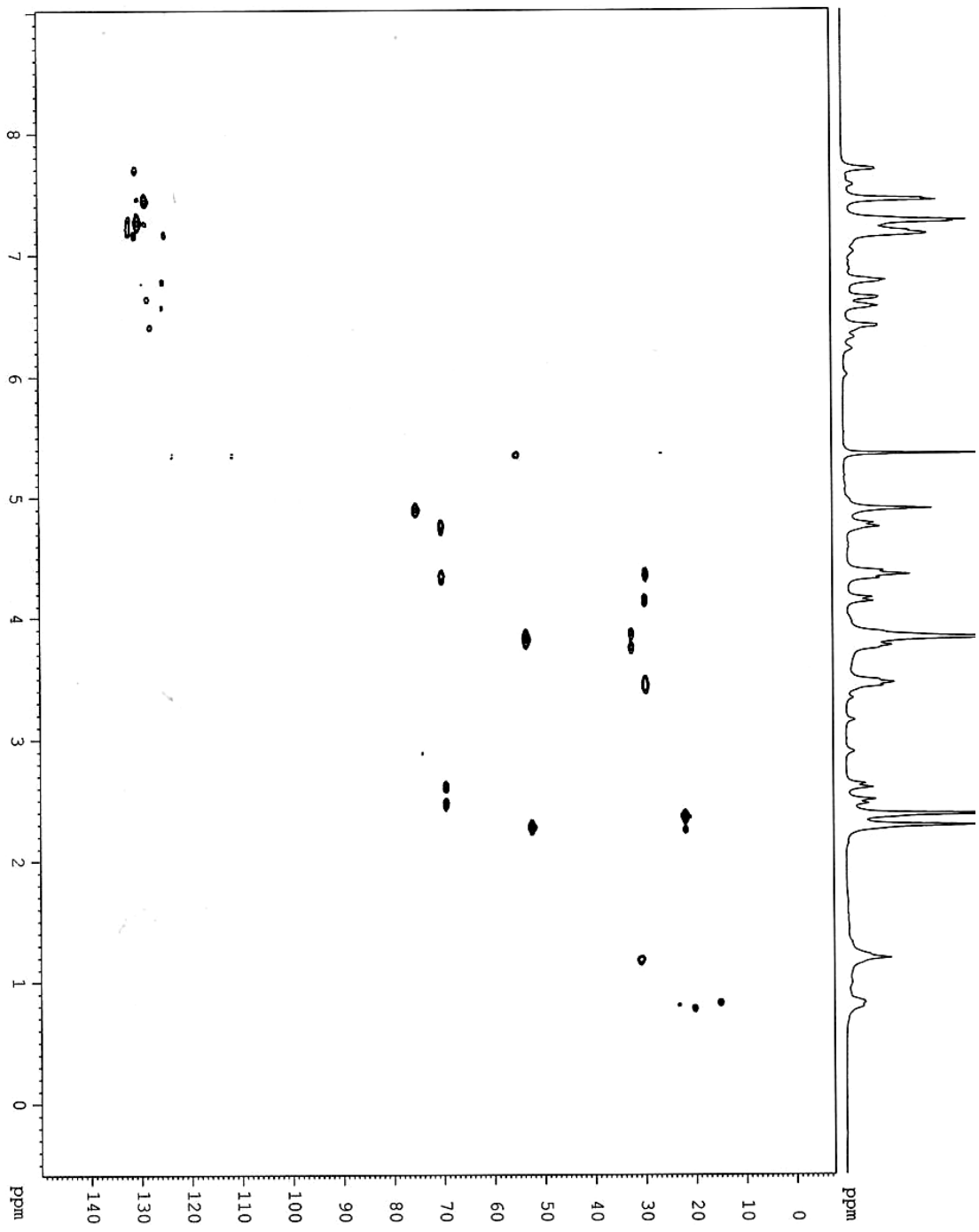
HMQC spectrum of **2a** (CD_2Cl_2, 188 K)



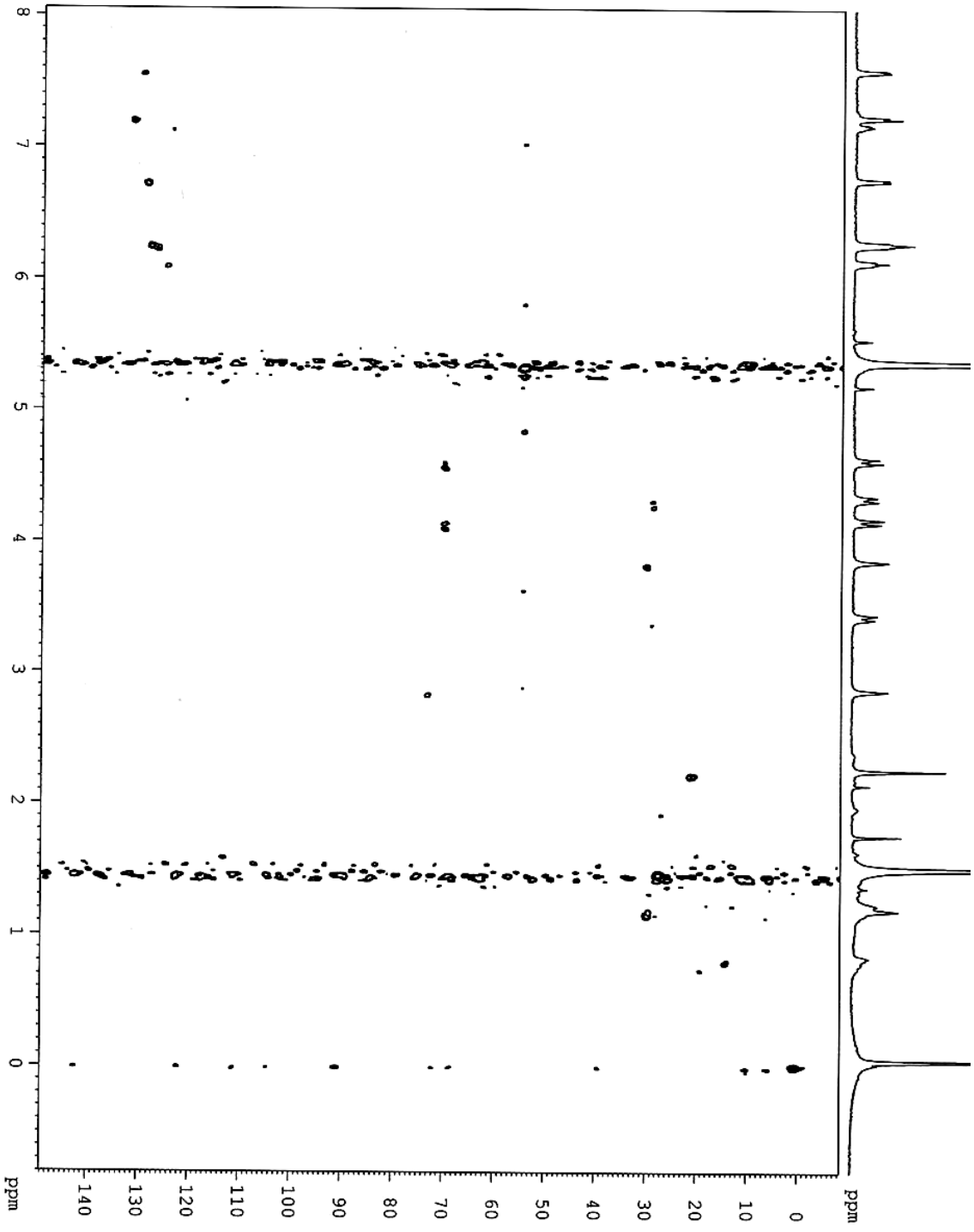
HMQC spectrum of **2b** (CD_2Cl_2, 188 K)



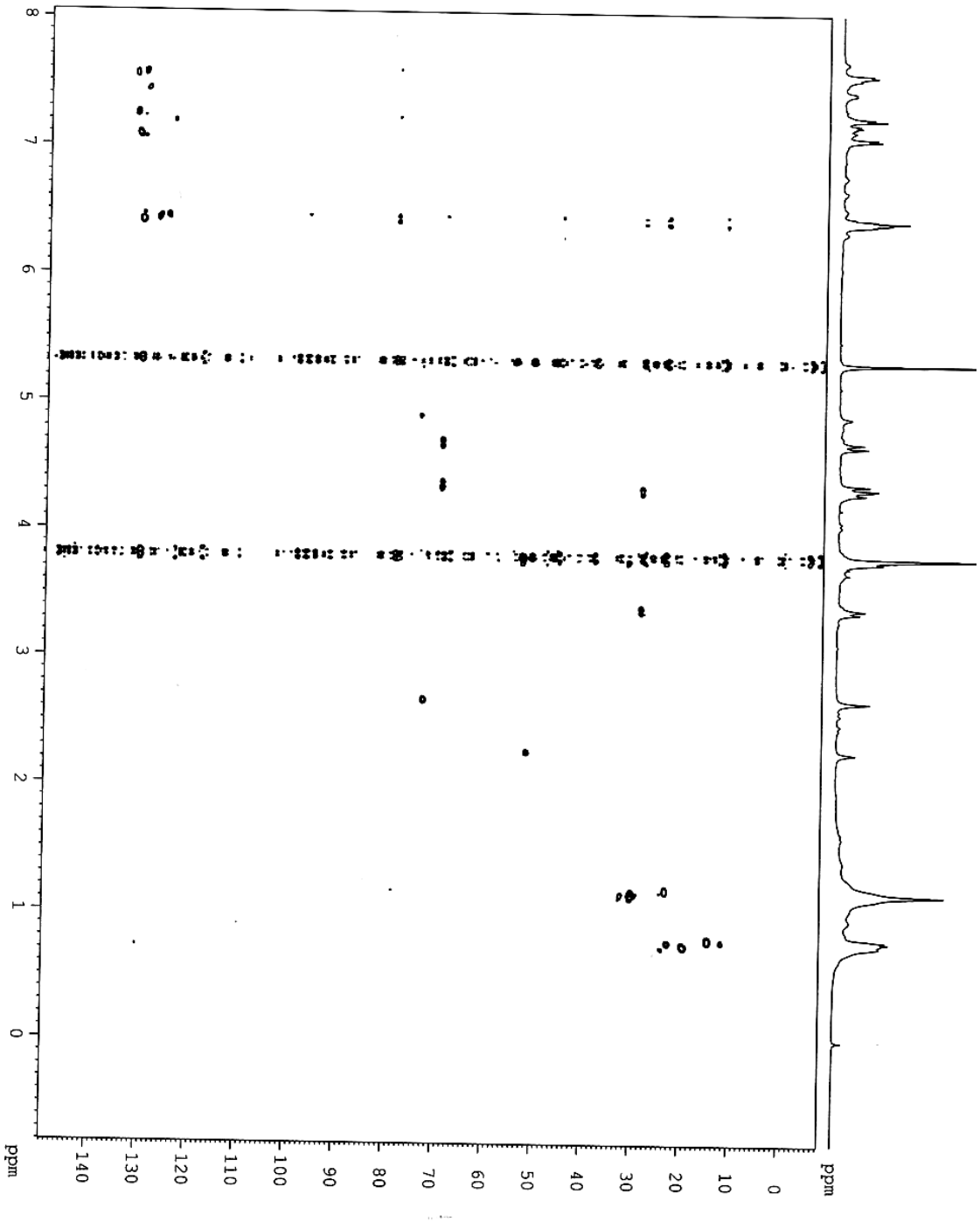
HMQC spectrum of **3a** (CD_2Cl_2, 188 K)



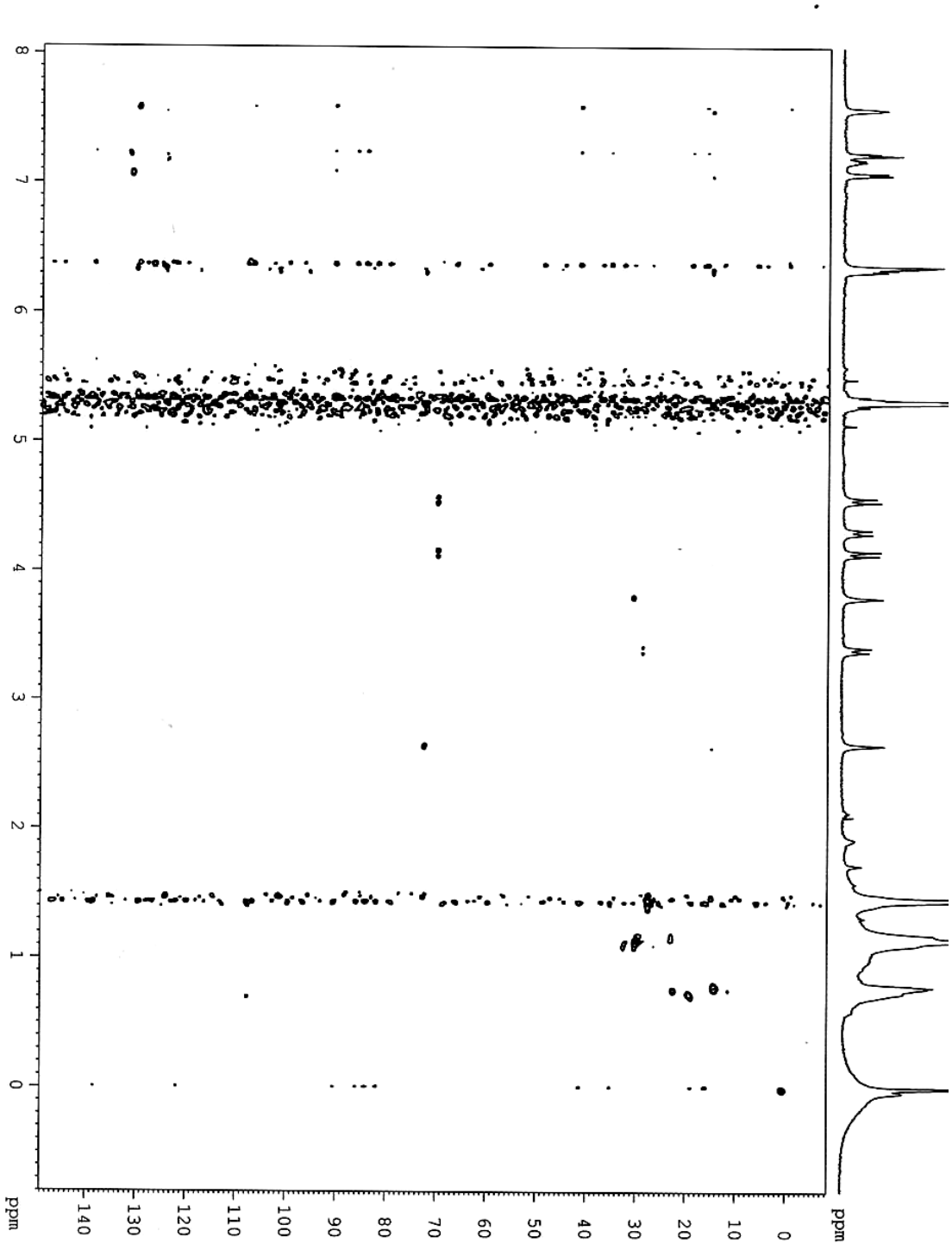
HMQC spectrum of **3b** (CD_2Cl_2, 188 K)



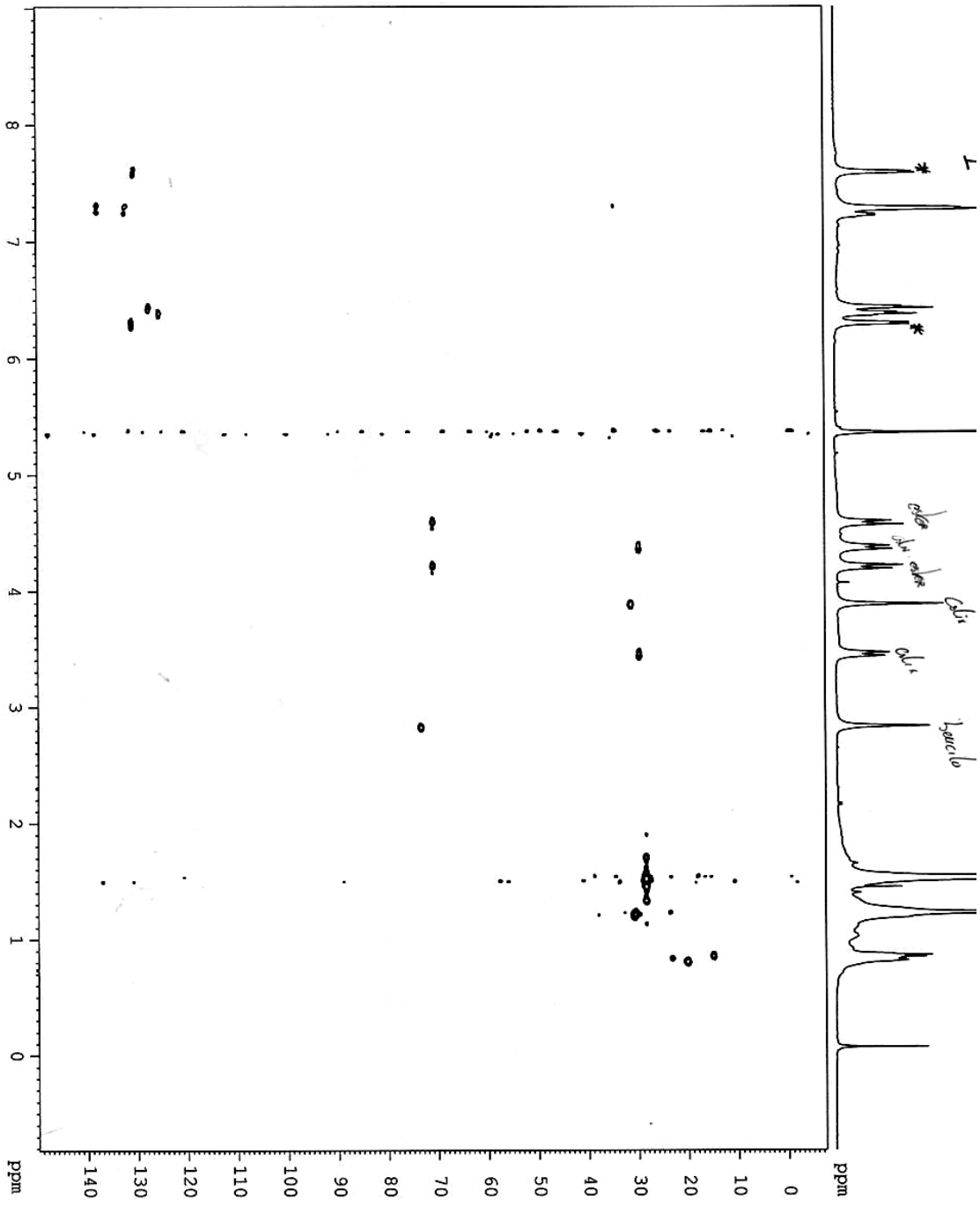
HMQC spectrum of **3c** (CD_2Cl_2, 188 K)



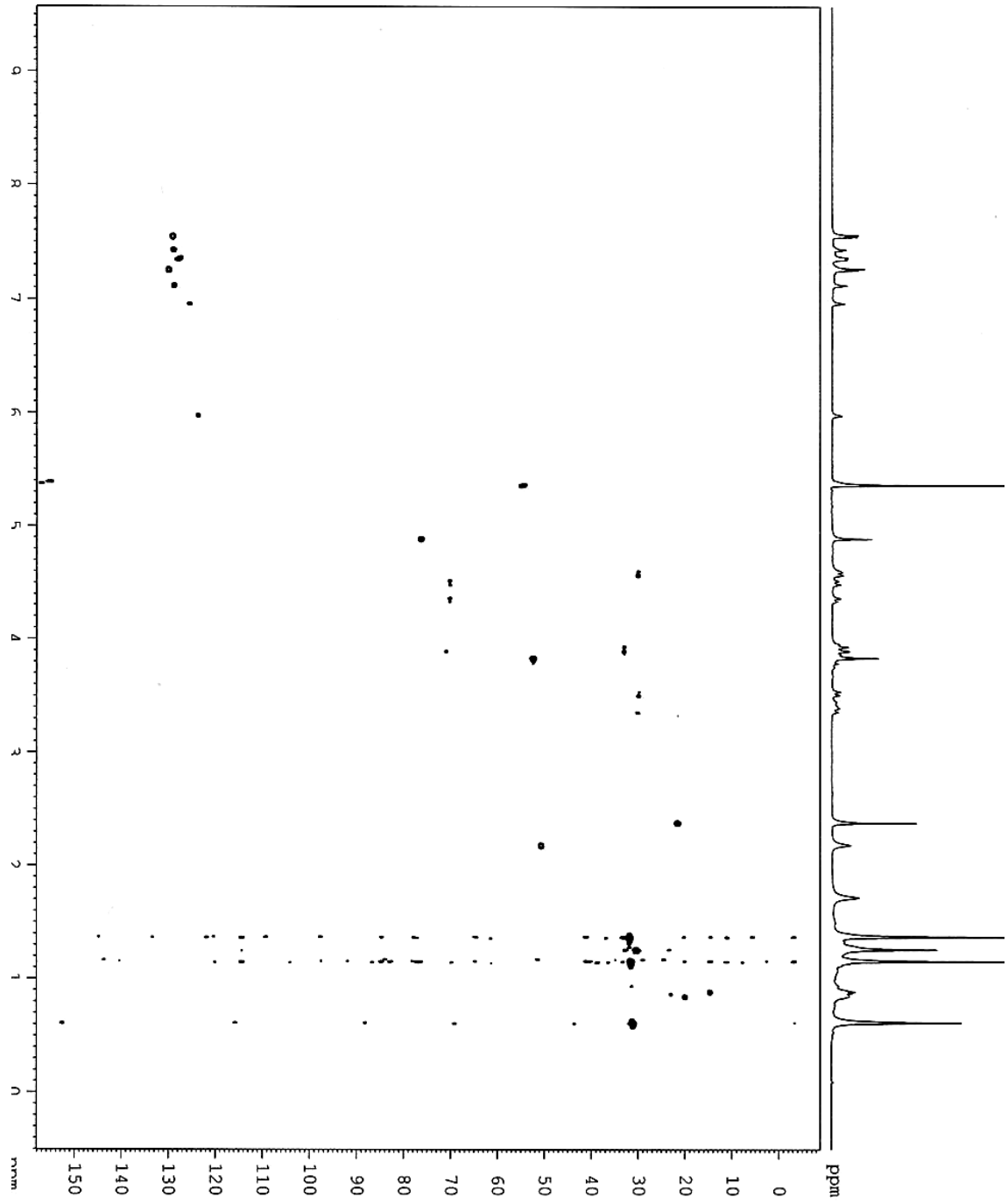
HMQC spectrum of **3d** (CD_2Cl_2, 188 K)



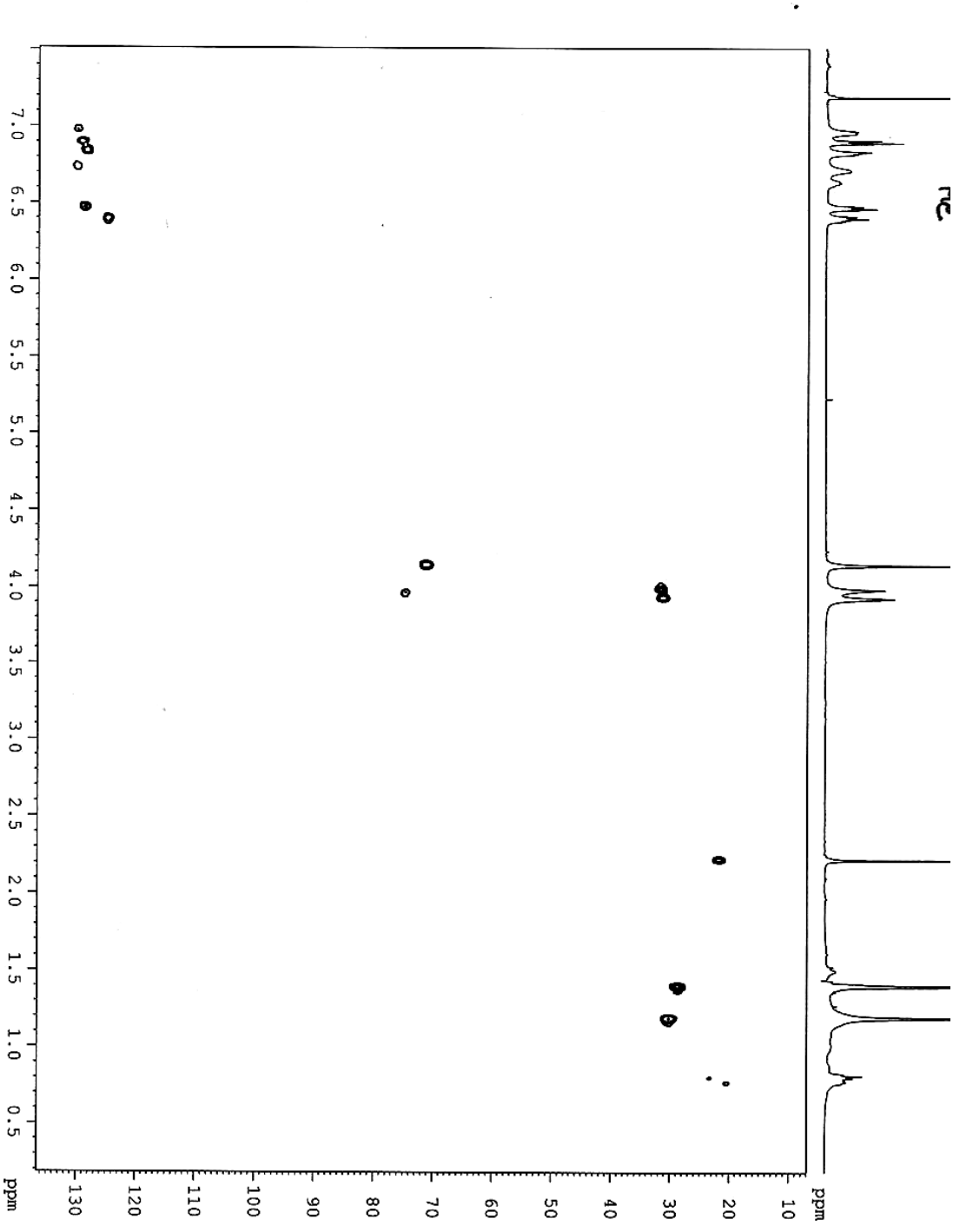
HMQC spectrum of **3f** (CD_2Cl_2, 188 K)



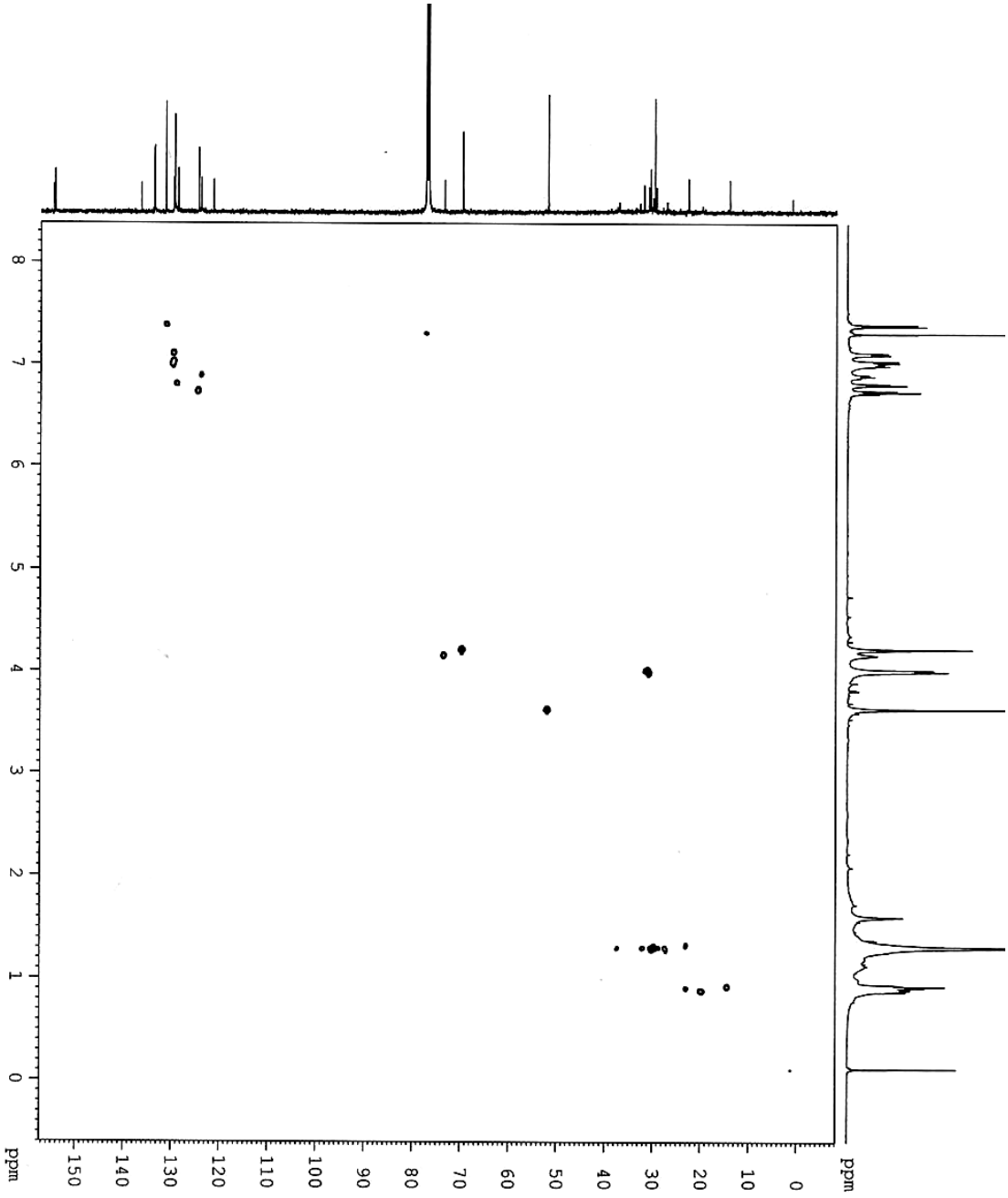
HMQC spectrum of **5a** (CD_2Cl_2, 248 K)



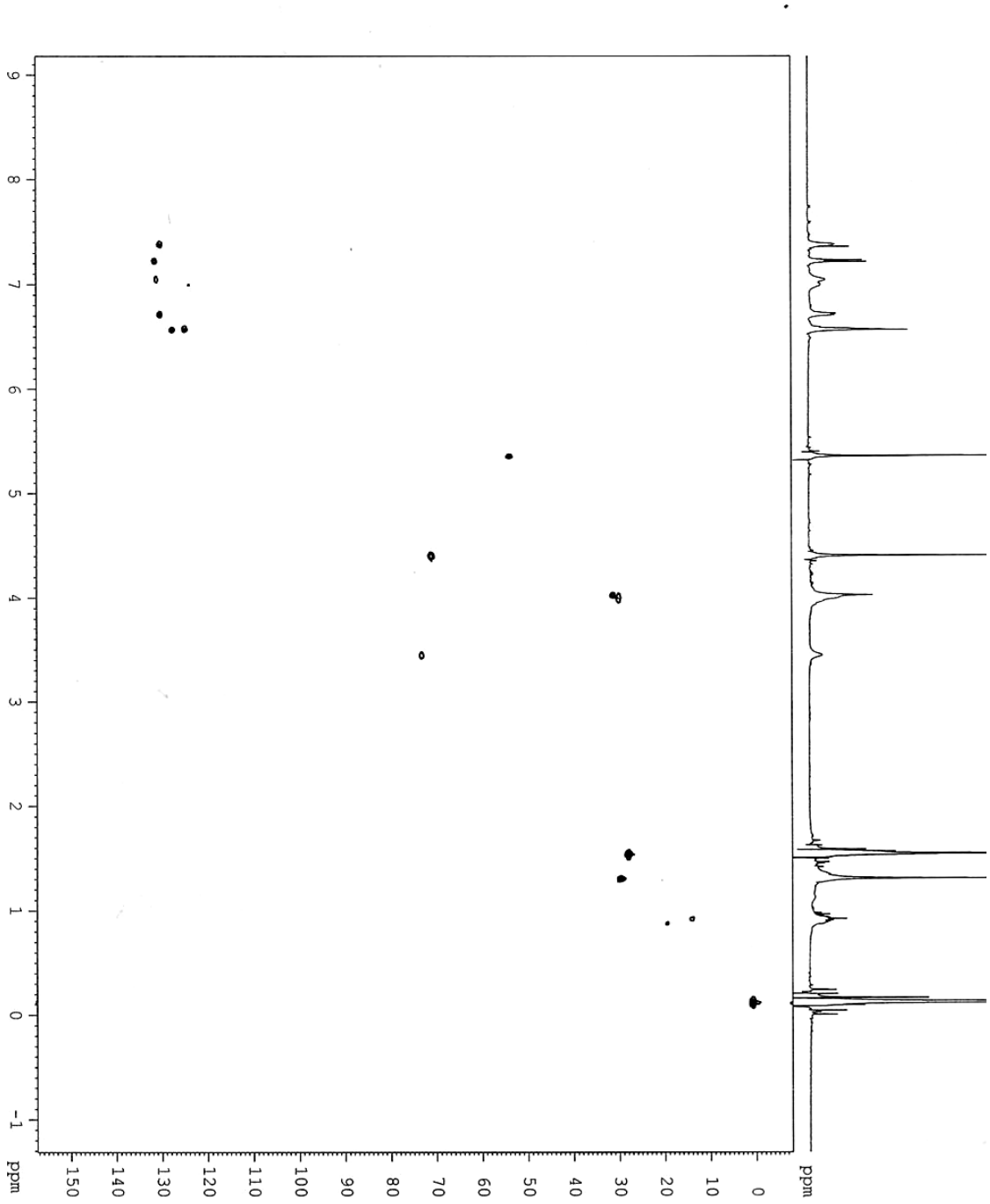
HMQC spectrum of **3b** ($CDCl_3$, 298 K)



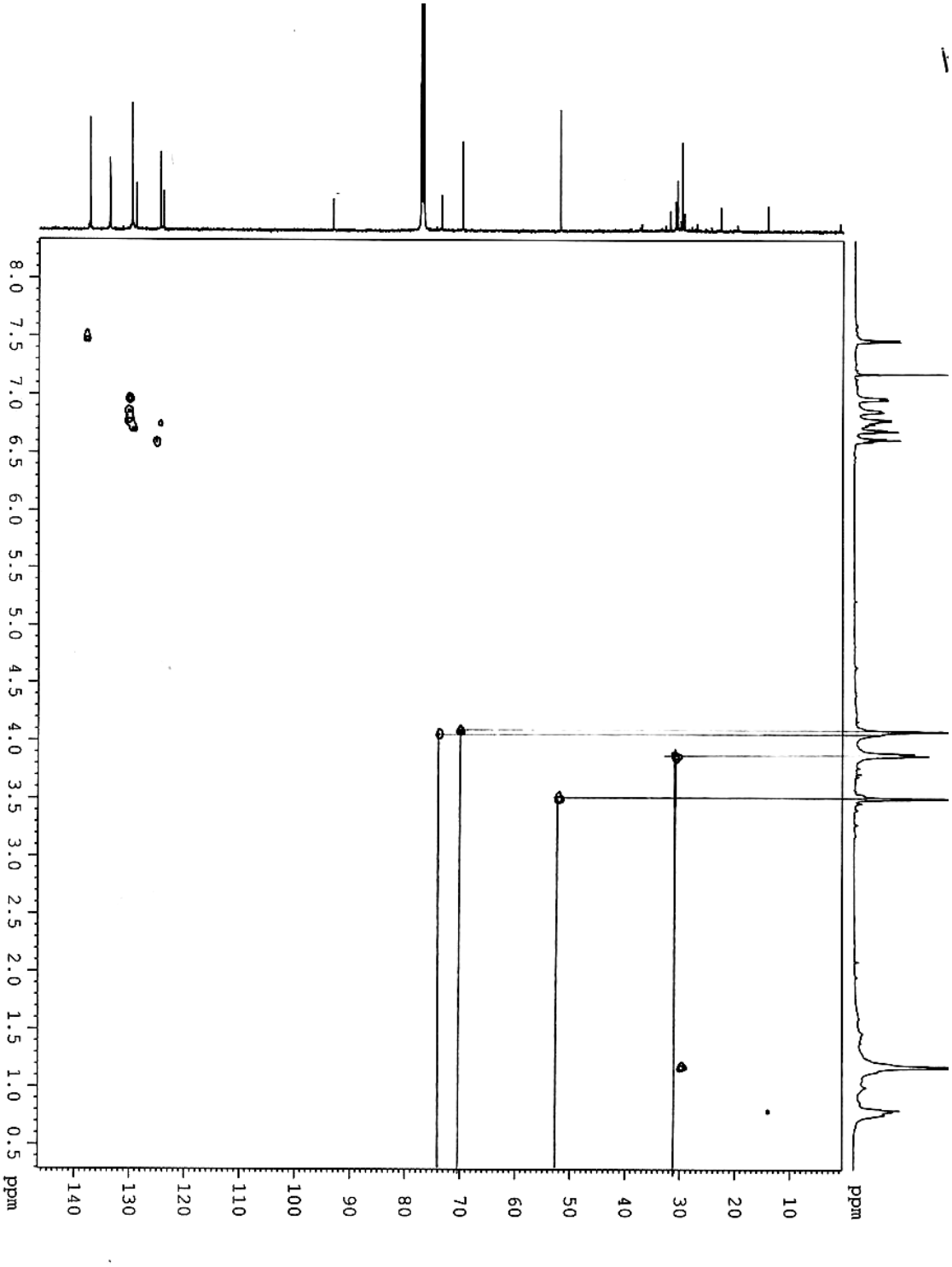
HMQC spectrum of **3c** ($CDCl_3$, 298 K)



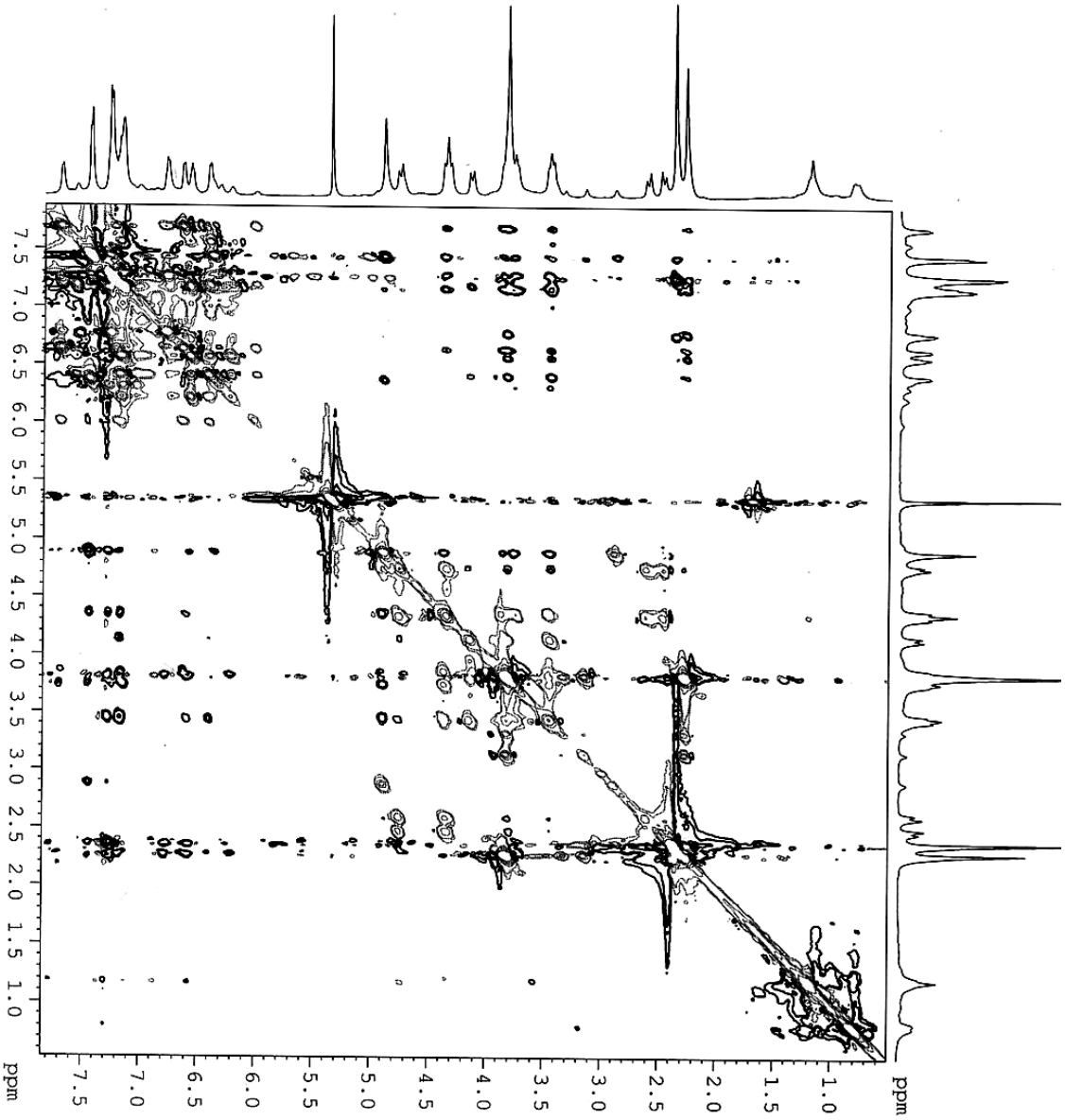
HMQC spectrum of **3d** ($CDCl_3$, 298 K)



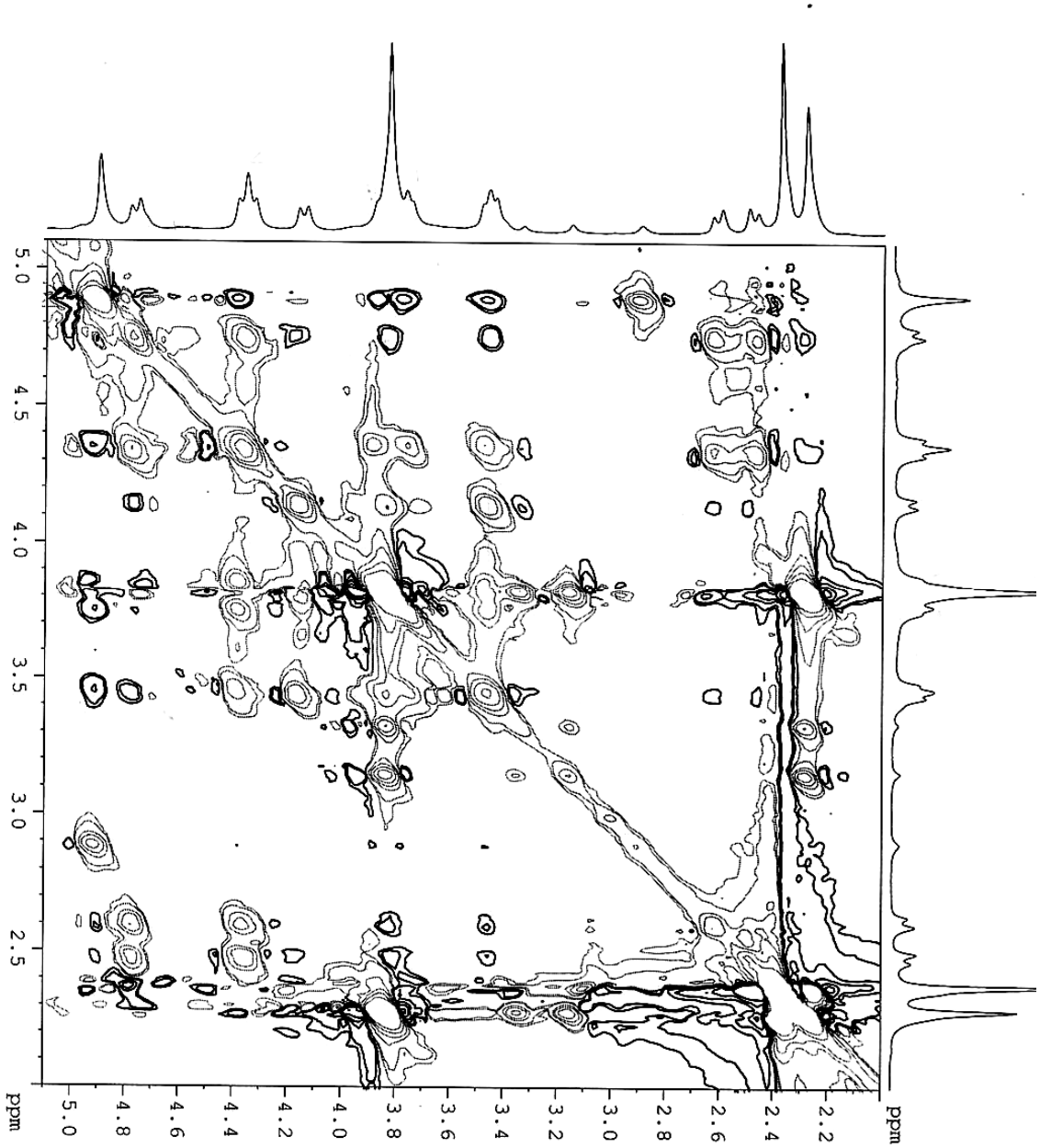
HMQC spectrum of **3e** ($CDCl_3$, 298 K)



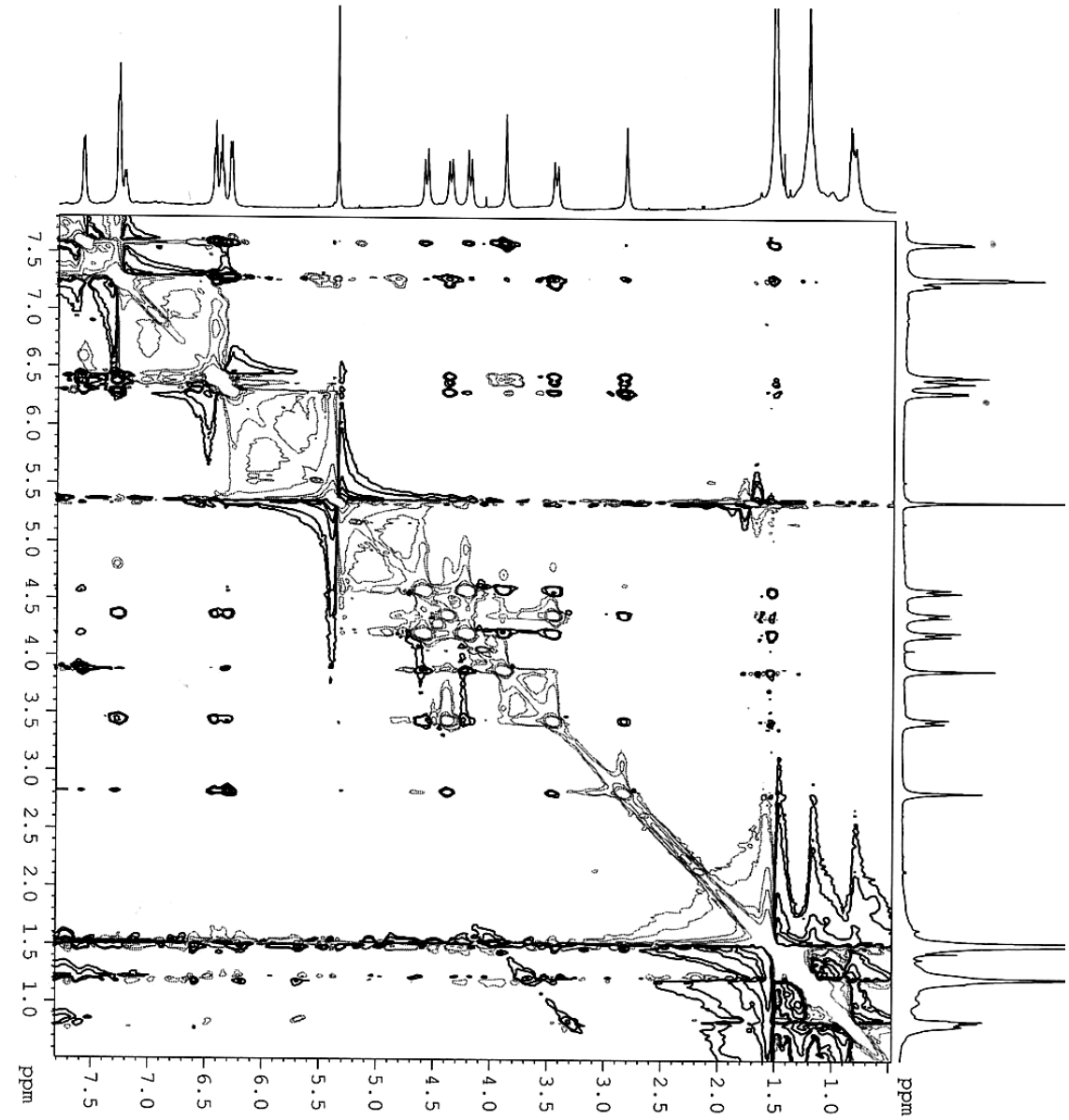
ROESY spectrum of **3a** (CD_2Cl_2, 188 K)



Partial ROESY spectrum of **3a** (CD_2Cl_2, 188 K)



ROESY spectrum of **3f** (CD_2Cl_2, 188 K)



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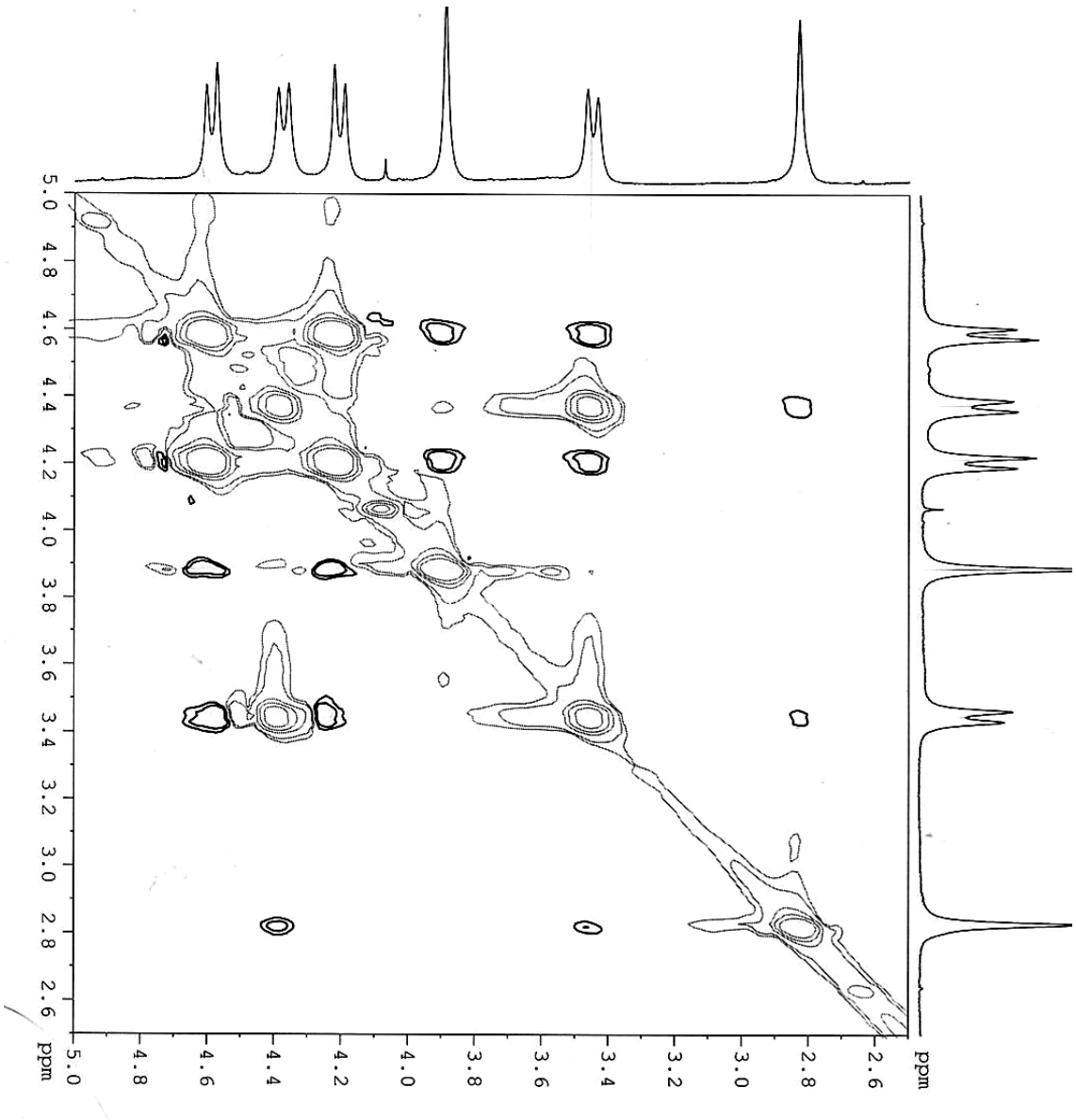
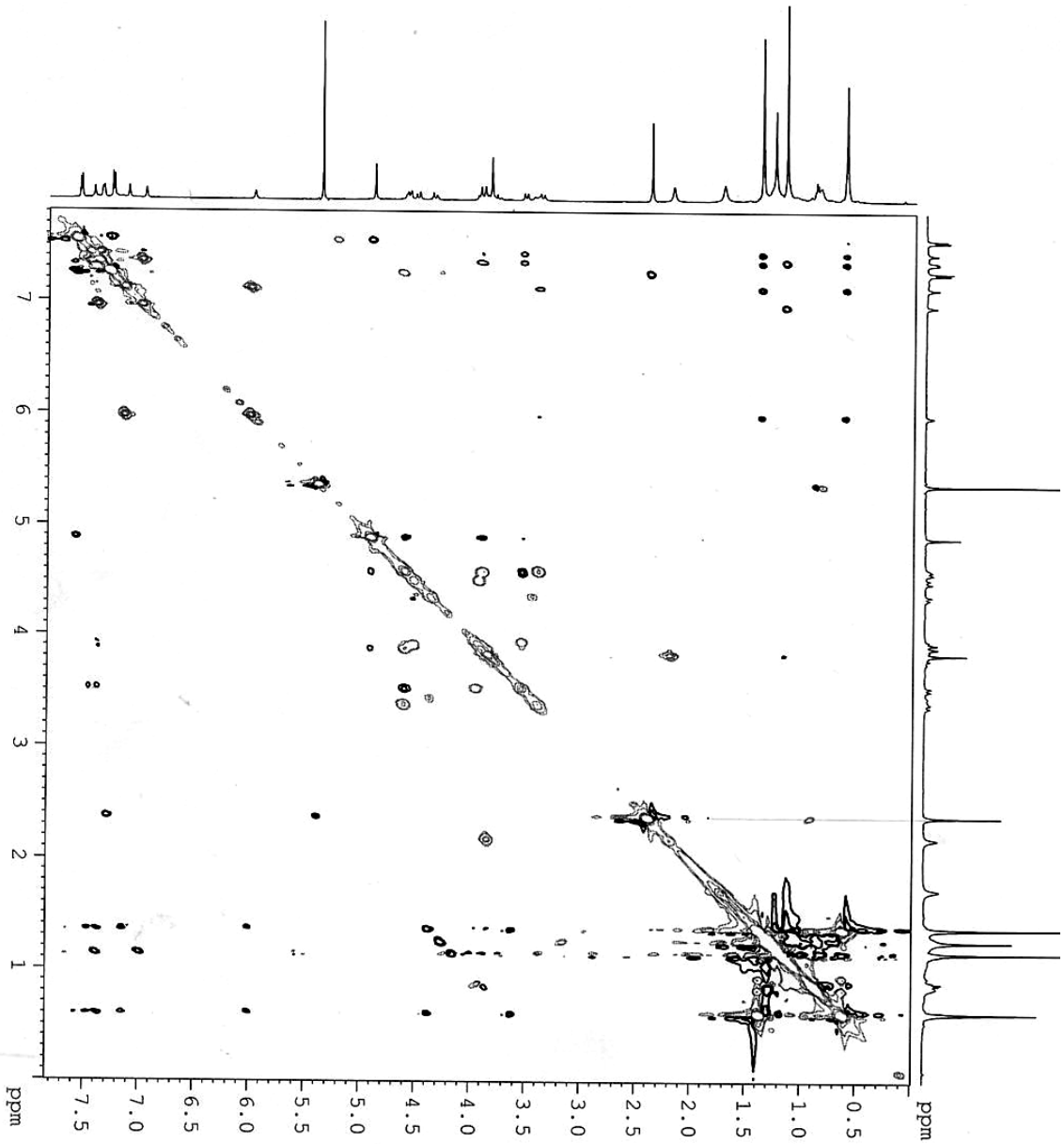
Partial ROESY spectrum of **3f** (CD_2Cl_2, 188 K)



ROESY spectrum of **5a** (CD_2Cl_2, 248 K)



Partial ROESY spectrum of **5a** (CD_2Cl_2, 248 K)