Supplementary Material

Complexation of imidazopyridine-based cations with a 24-crown-8 ether host: [2]pseudorotaxane and partially-threaded structures.

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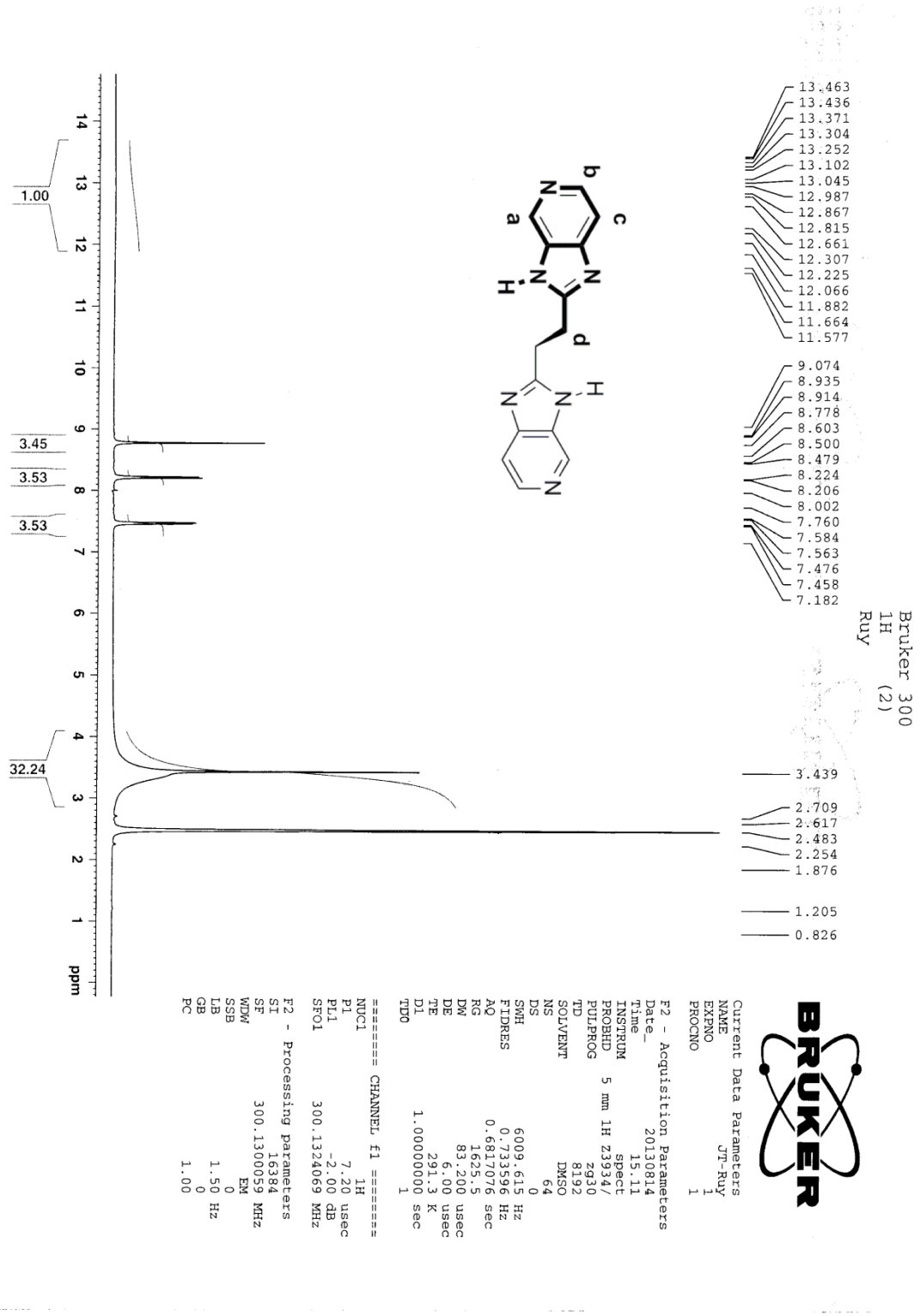
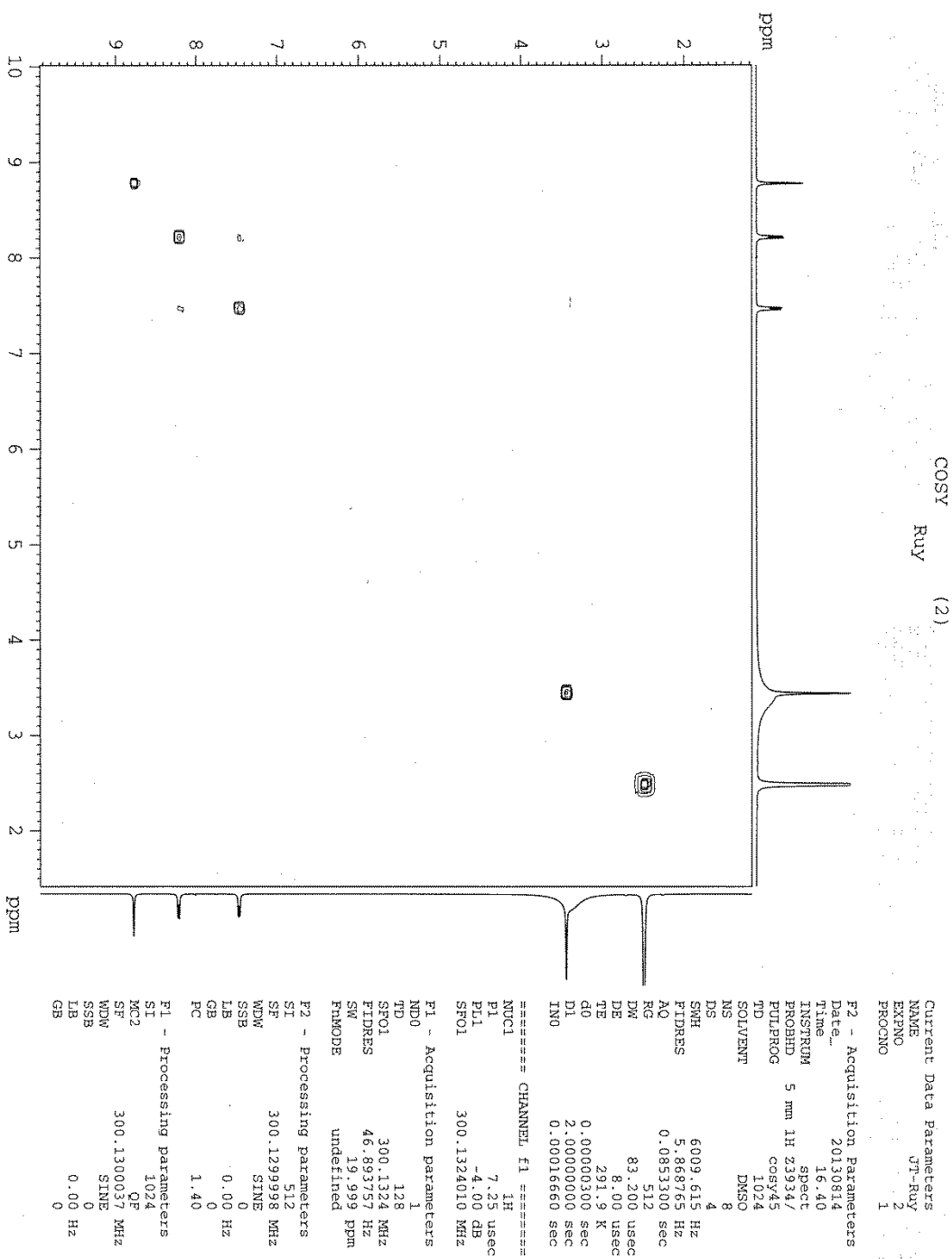
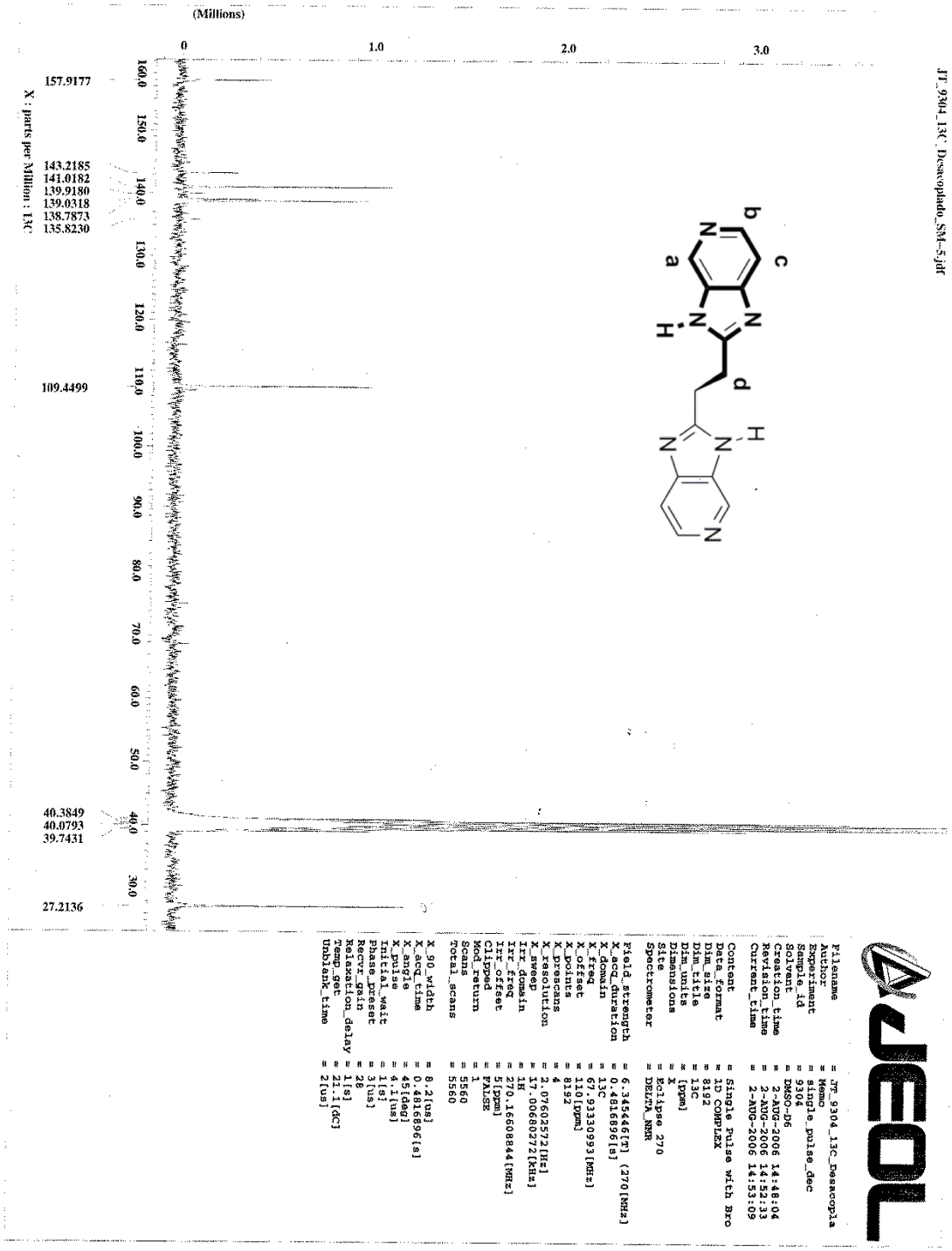
Compound **[2]** ^{1}H NMR (DMSO-d_6, 300 MHz)



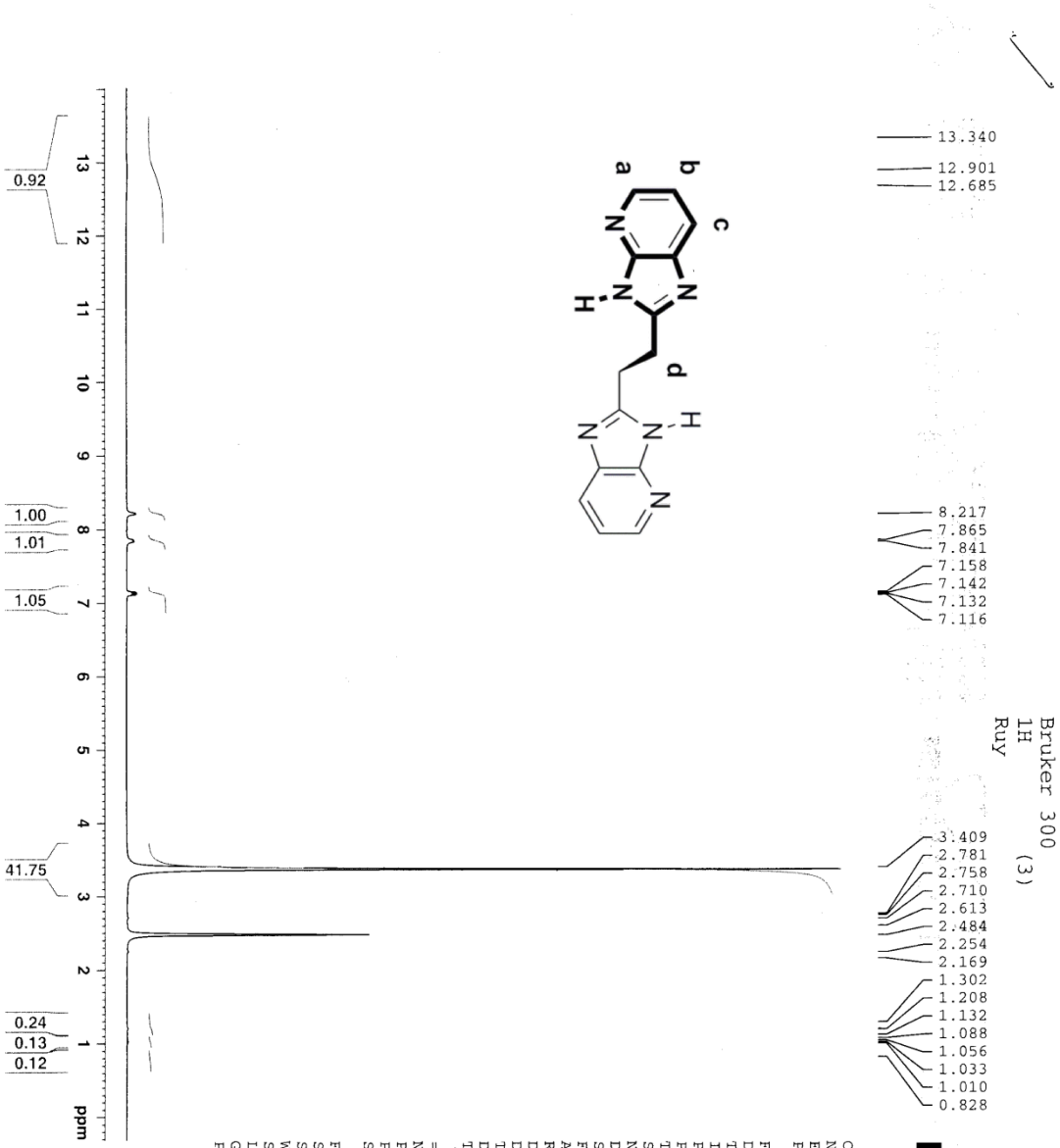
Compound **[2]** COSY ^{1}H-^{1}H NMR (DMSO-d_6, 300 MHz)



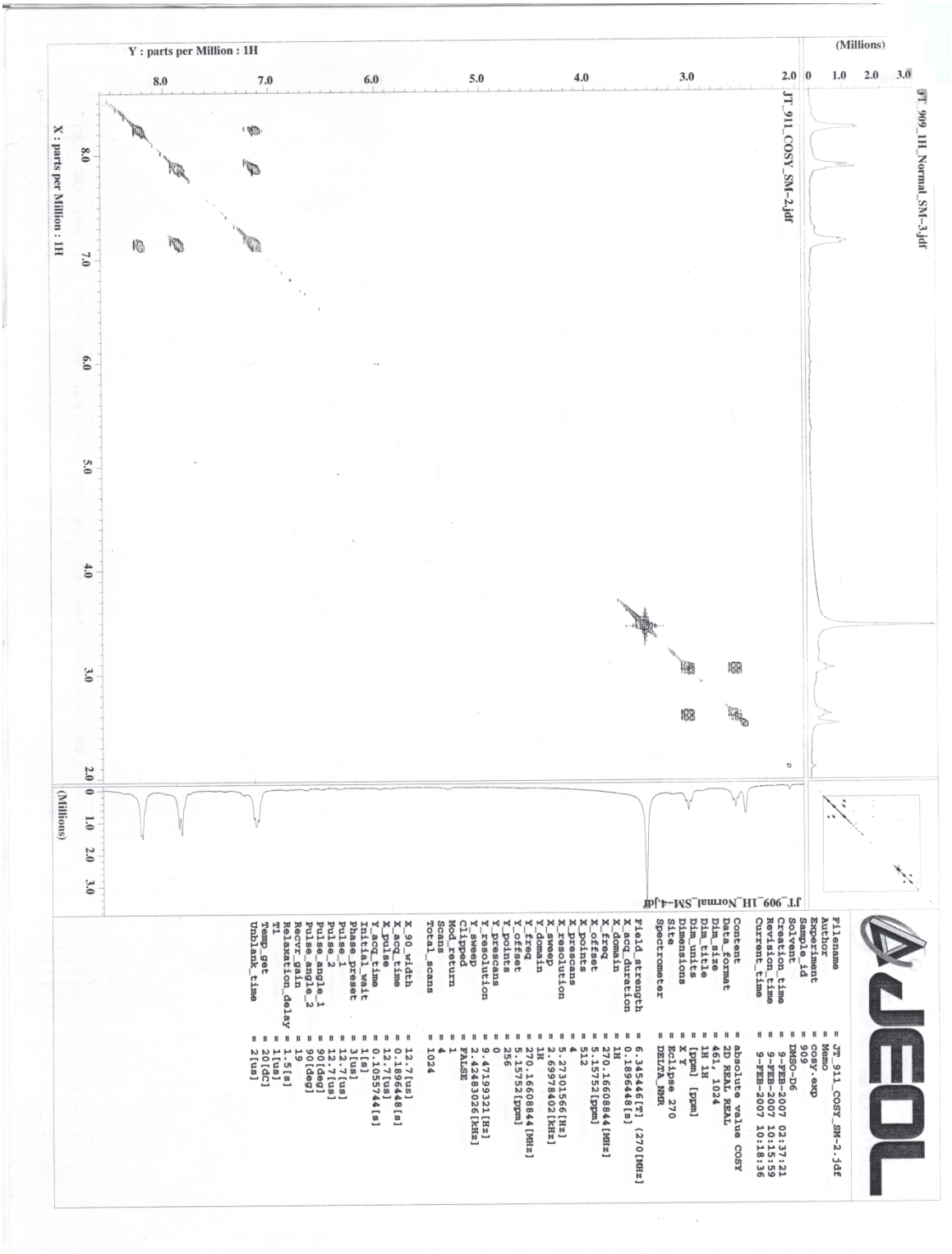
Compound **[2]** ^{13}C NMR (DMSO-d_6, 68 MHz)



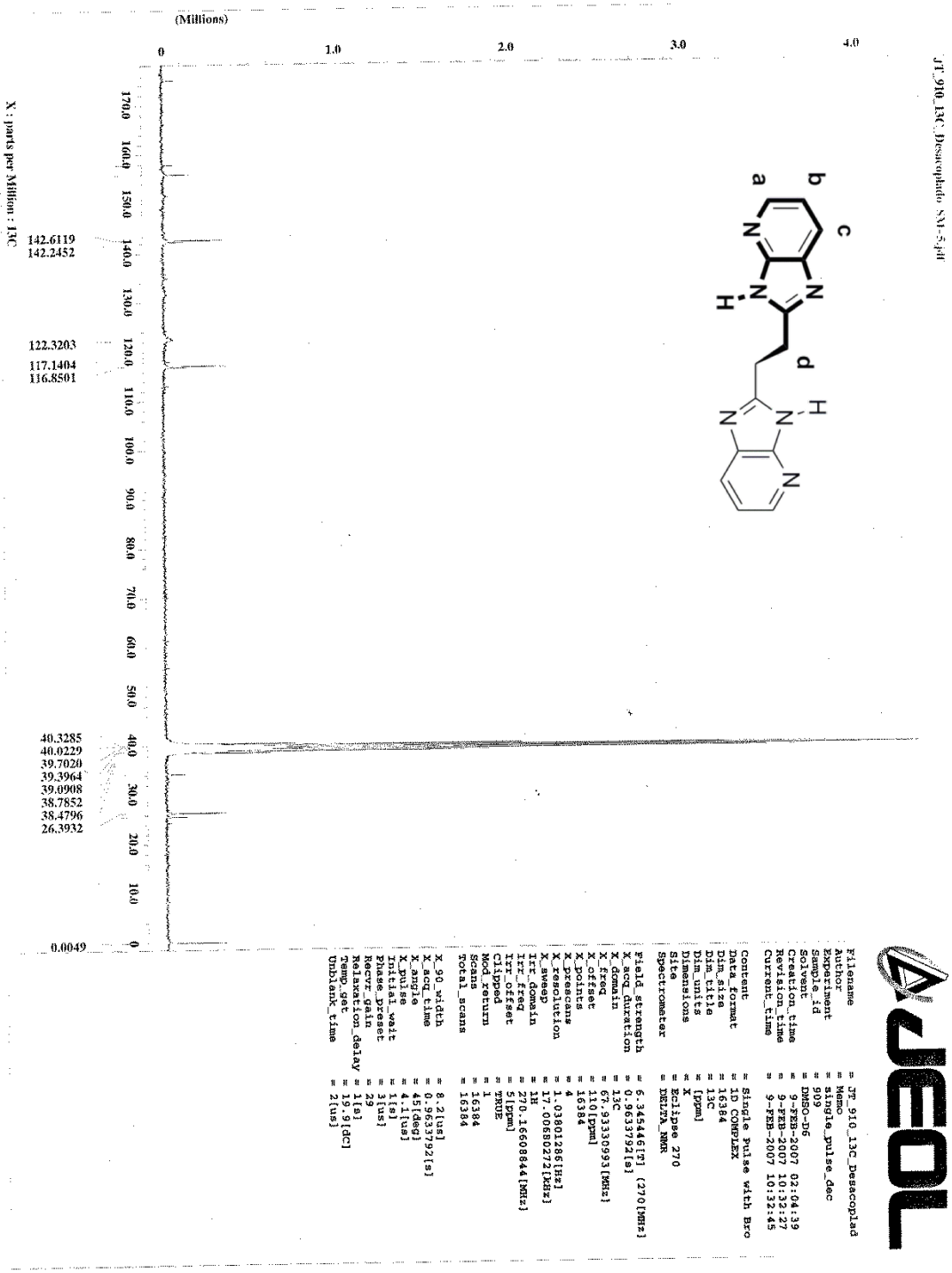
Compound **[3]** ^{1}H NMR (DMSO-d_6, 300 MHz)



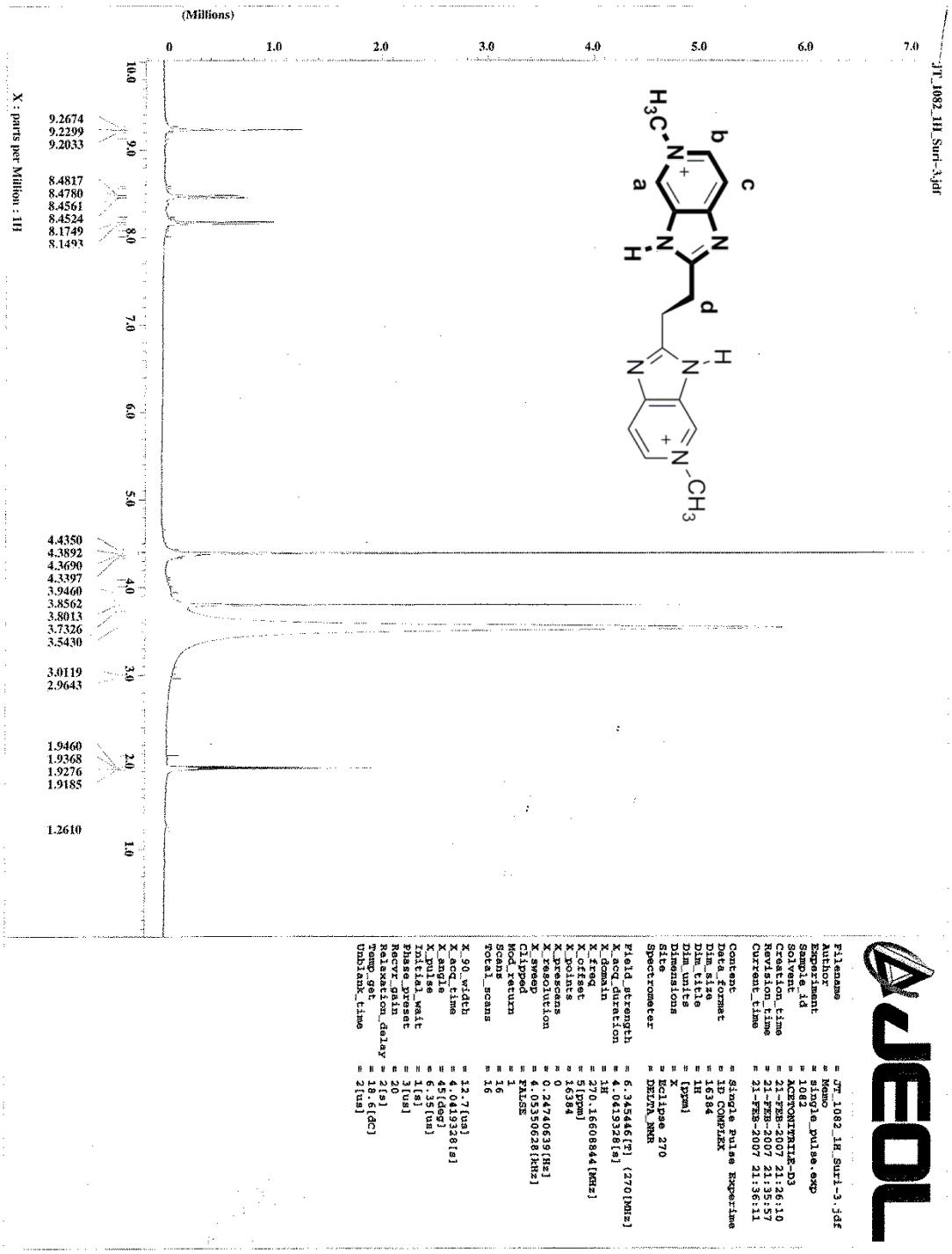
Compound **[3]** COSY ^{1}H-^{1}H NMR (DMSO-d_6, 270 MHz)



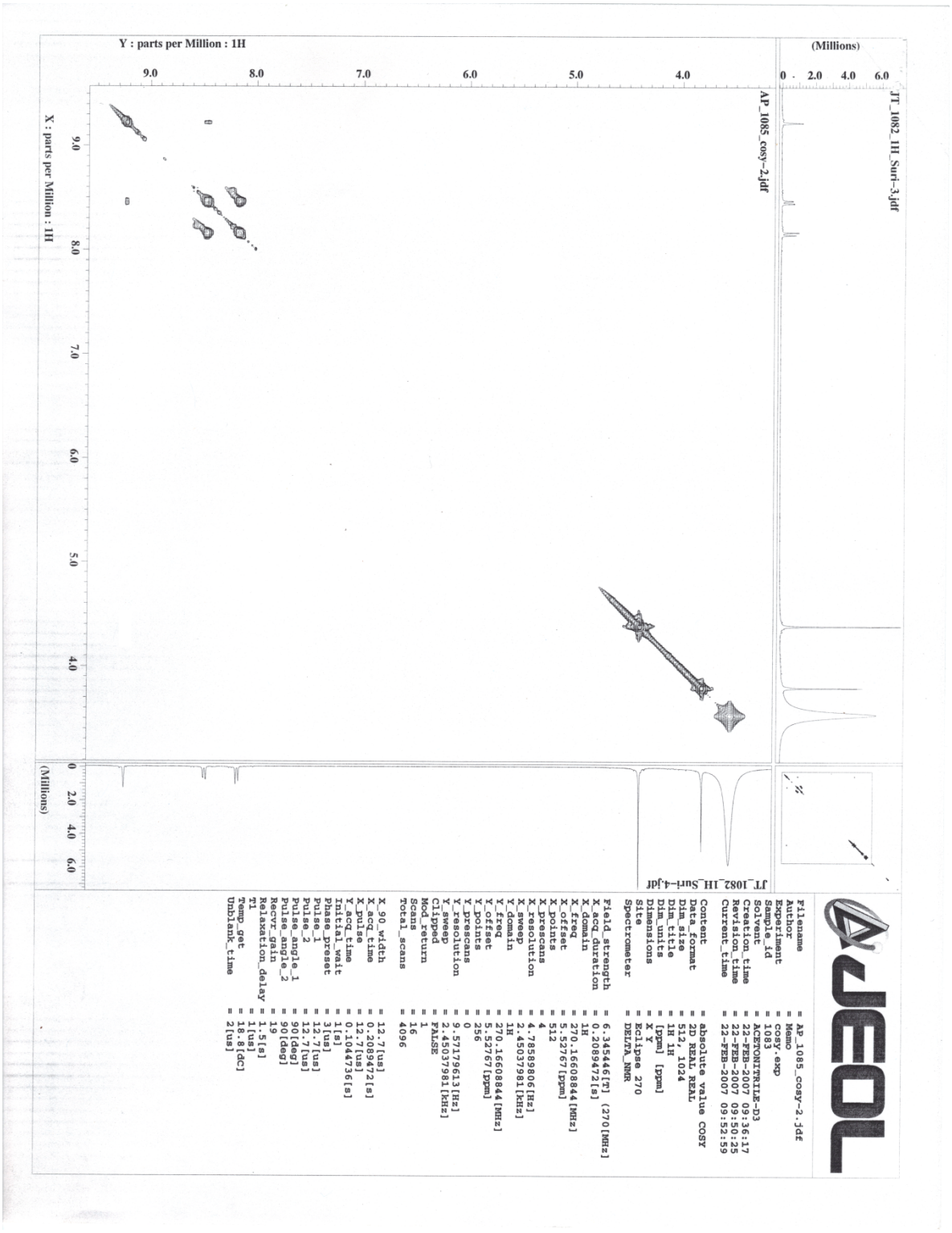
Compound **[3]** ^{13}C NMR (DMSO-d_6, 68 MHz)



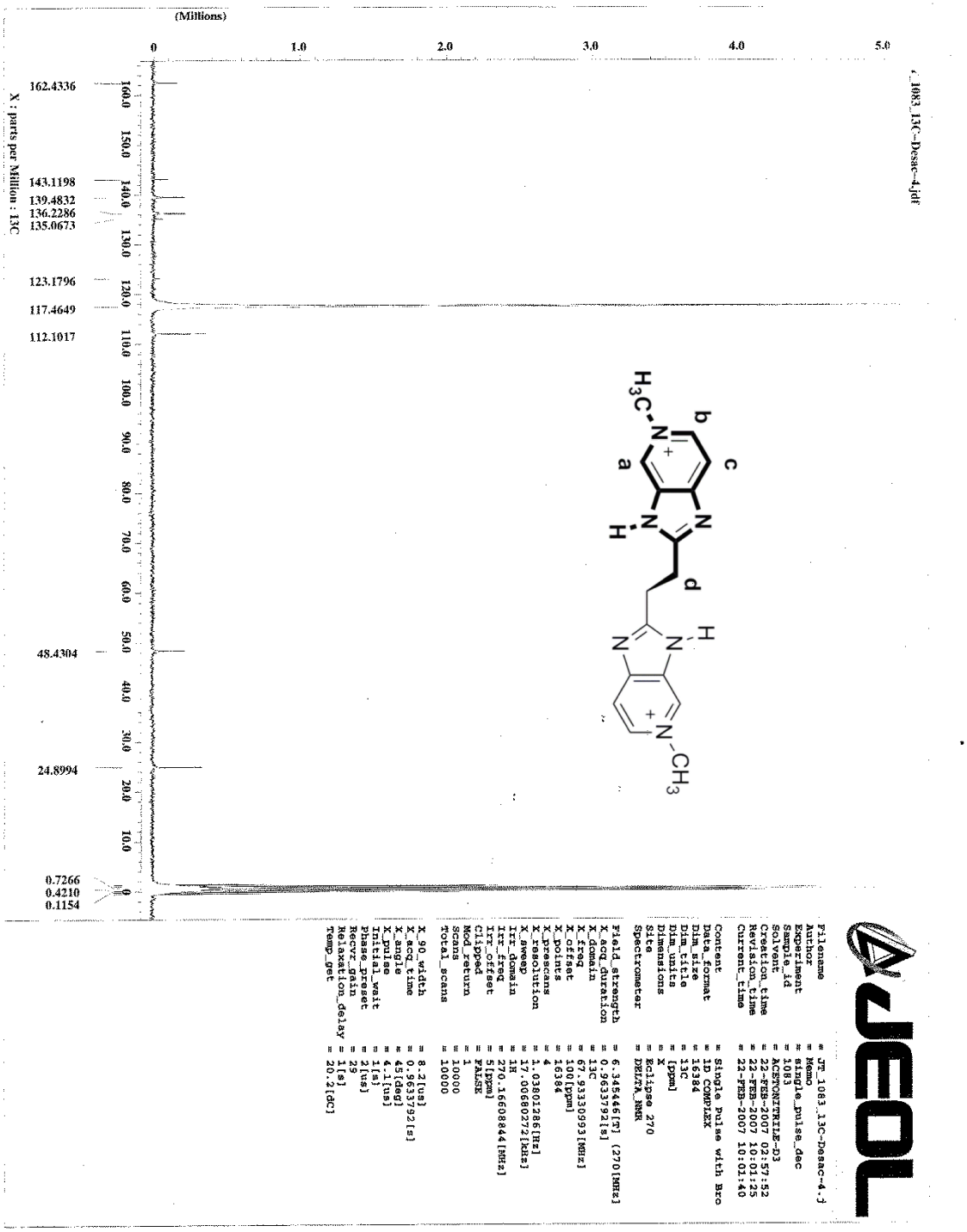
Compound **[2·Me$_2$][CF$_3$SO$_3$]$_2$** ^{1}H NMR (CD$_3$CN, 270 MHz)



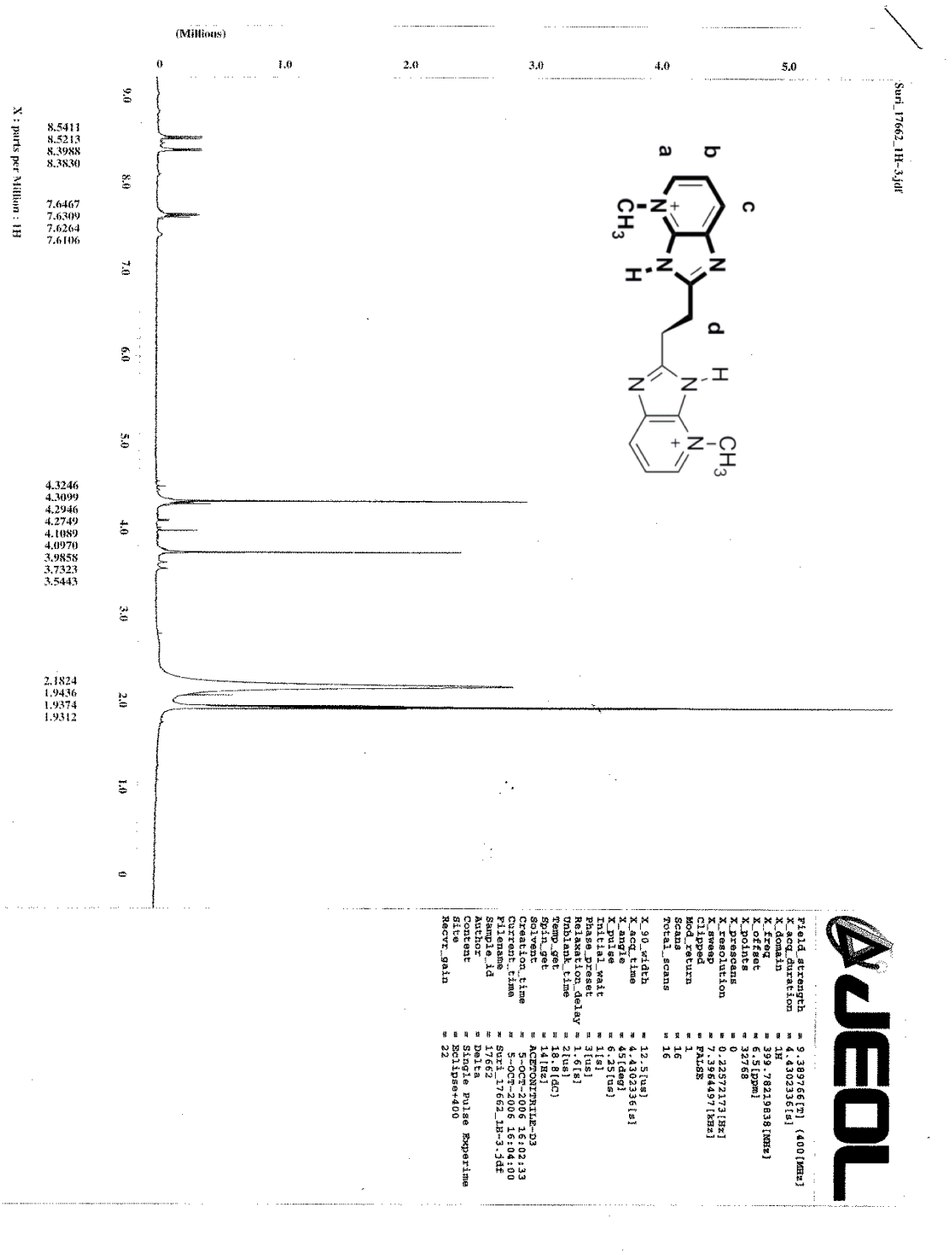
Compound **[2·Me$_2$][CF$_3$SO$_3$]$_2$** COSY ^{1}H-^{1}H NMR (CD$_3$CN, 270 MHz)



Compound **[2·Me$_2$][CF$_3$SO$_3$]$_2$** ^{13}C NMR (CD$_3$CN, 68 MHz)



Compound **[3·Me$_2$][CF$_3$SO$_3$]$_2$** ^{1}H NMR (CD$_3$CN, 400 MHz)



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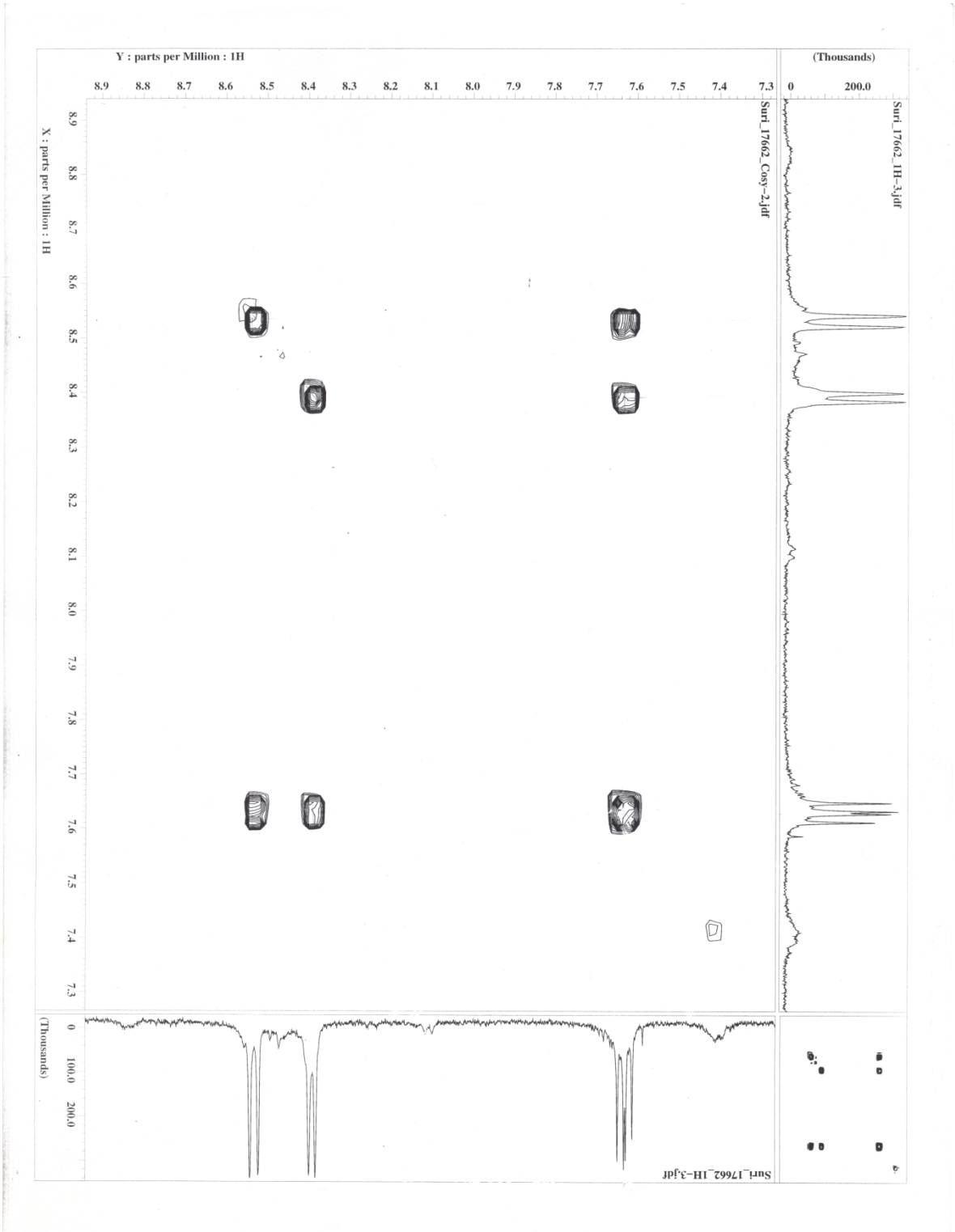

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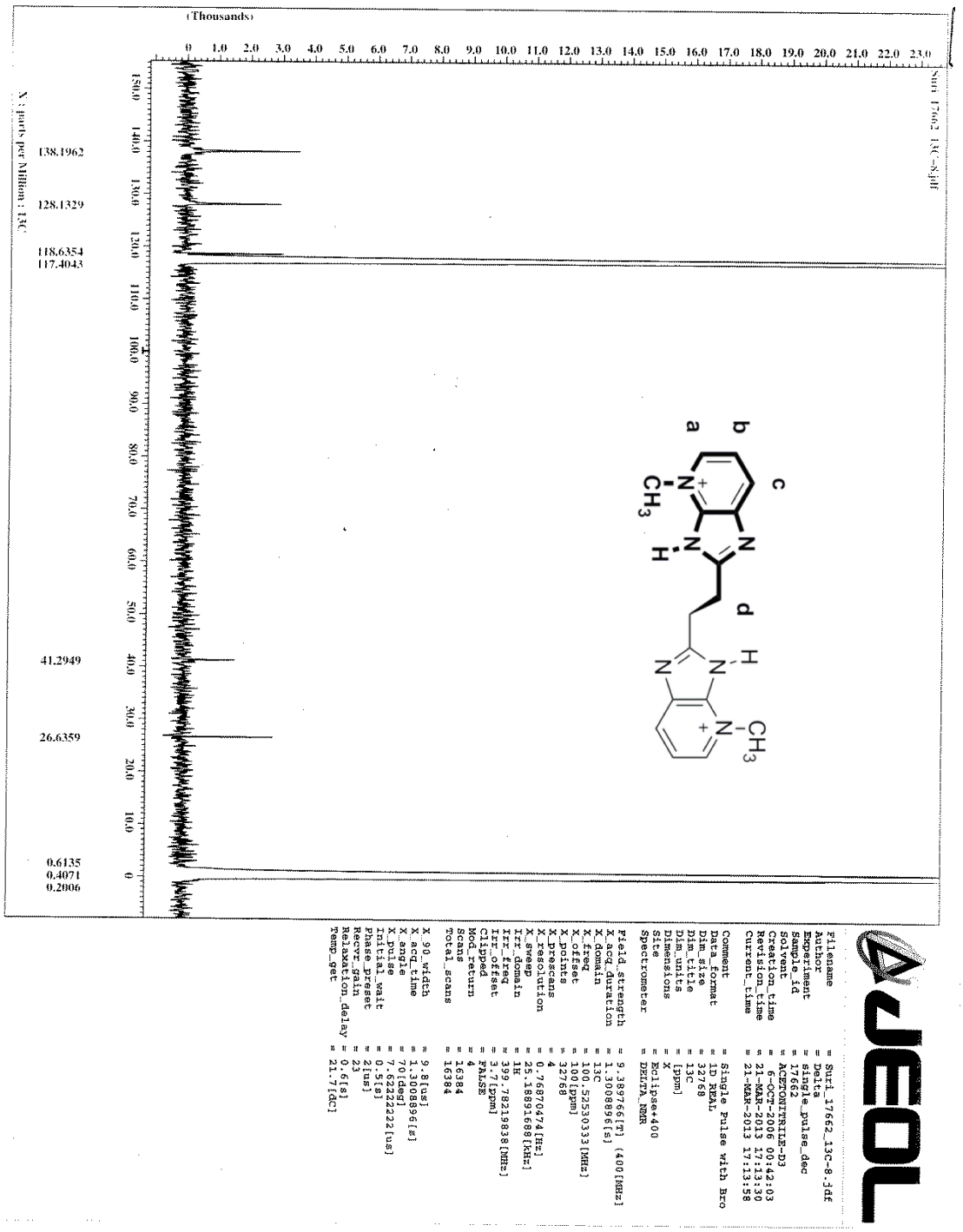

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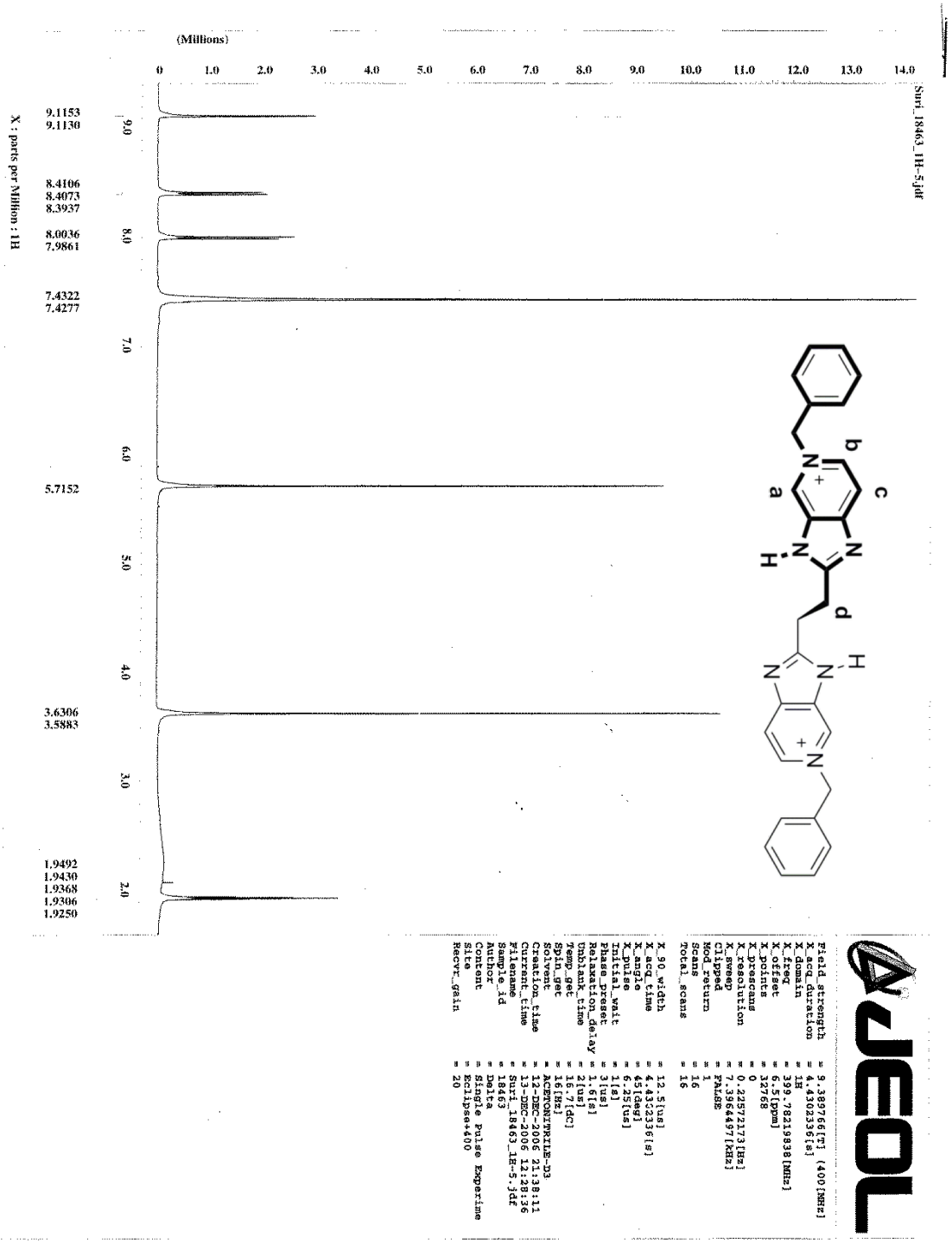
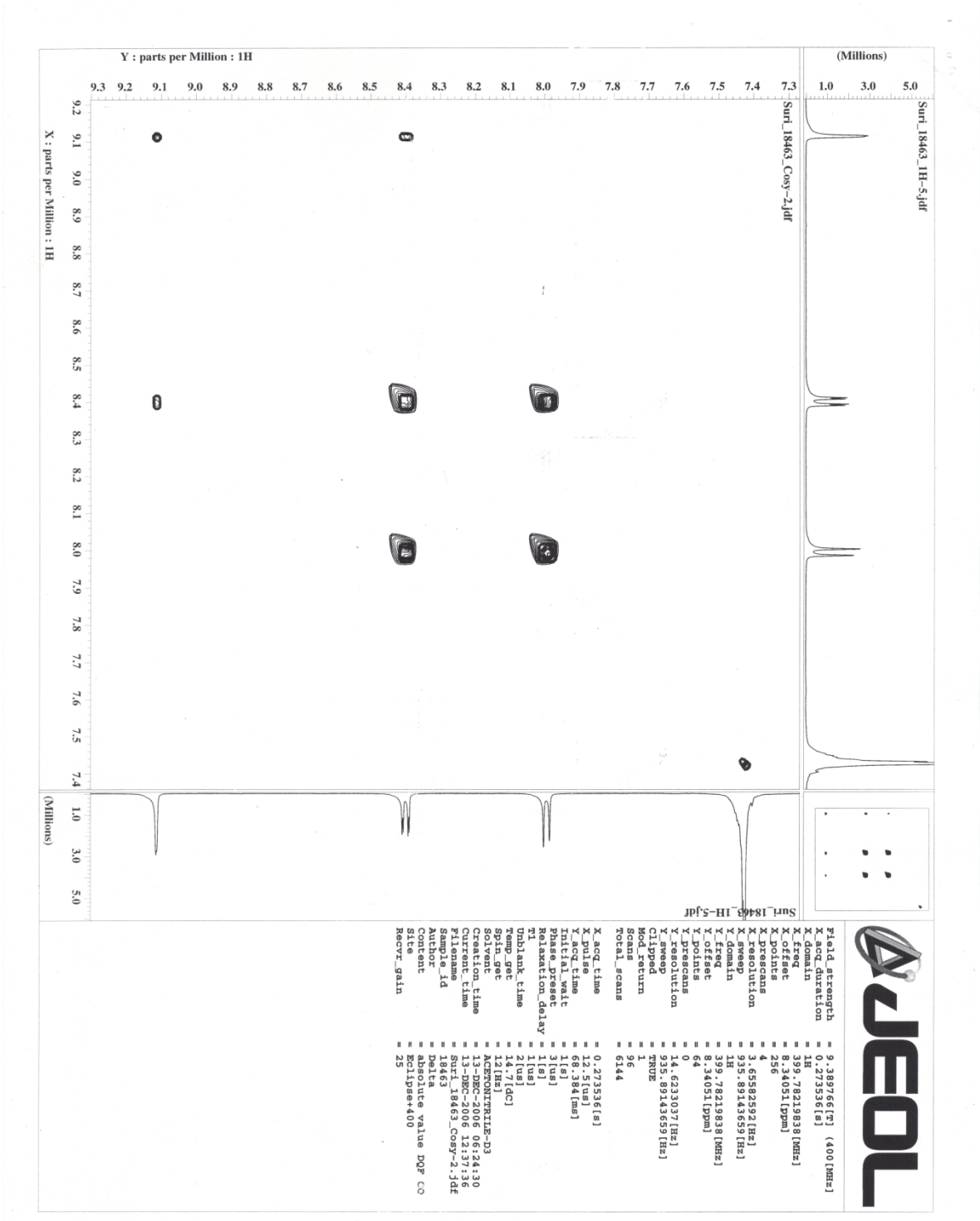
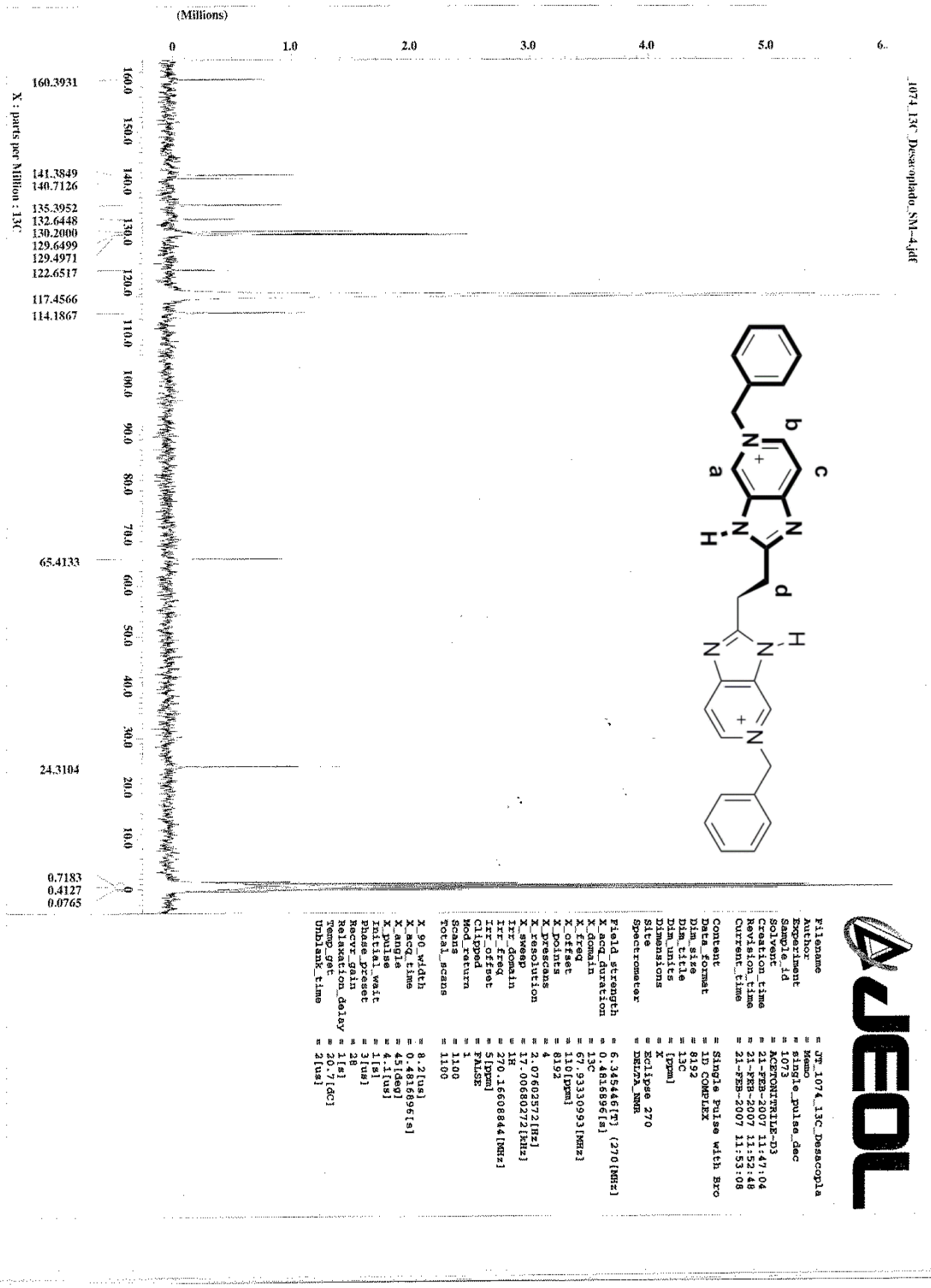


Compound **[2·Bn$_2$][CF$_3$SO$_3$]$_2$** COSY ^{1}H-^{1}H NMR (CD$_3$CN, 400 MHz)



Compound **[2·Bn$_2$][CF$_3$SO$_3$]$_2$** ^{13}C NMR (CD$_3$CN, 68 MHz)



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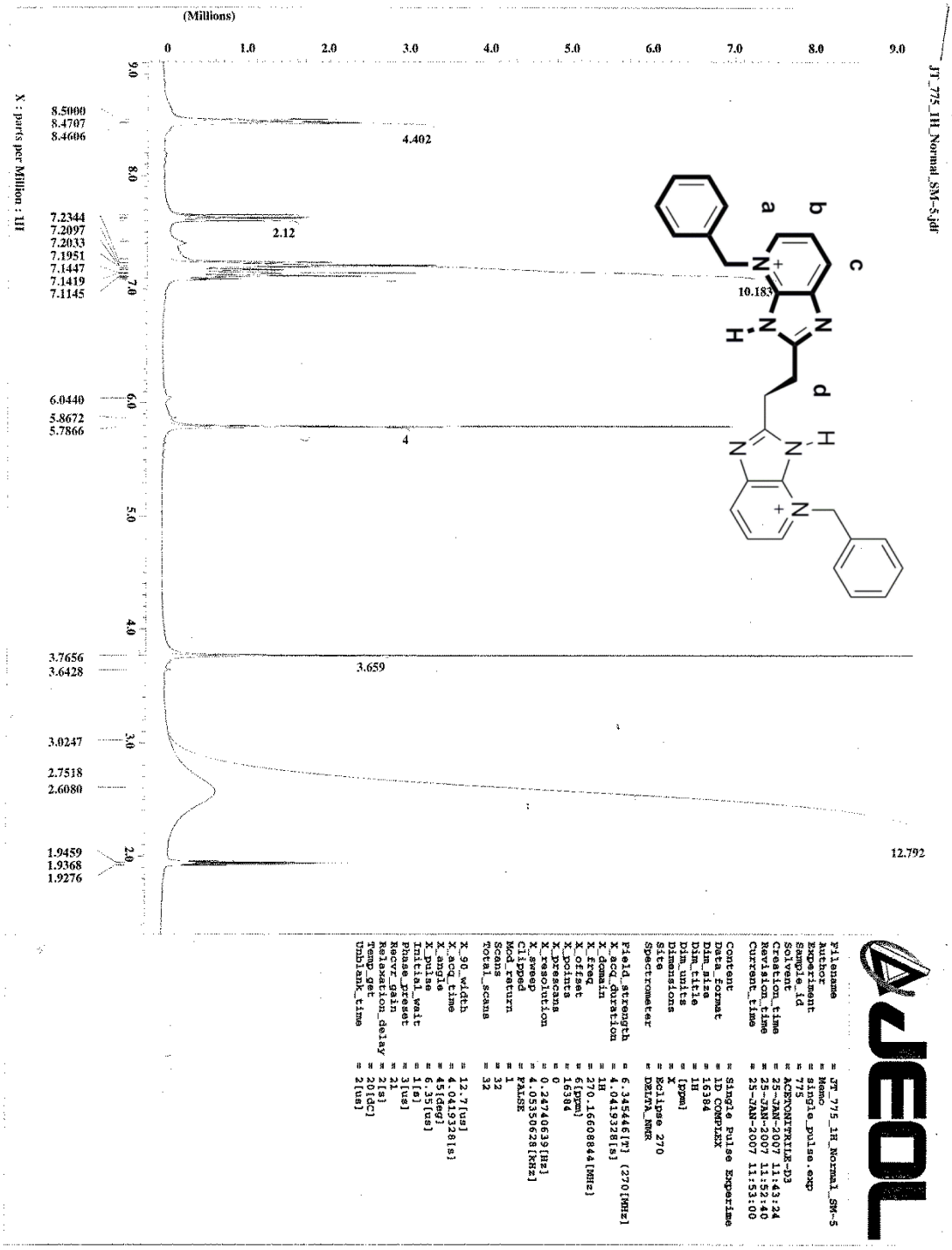

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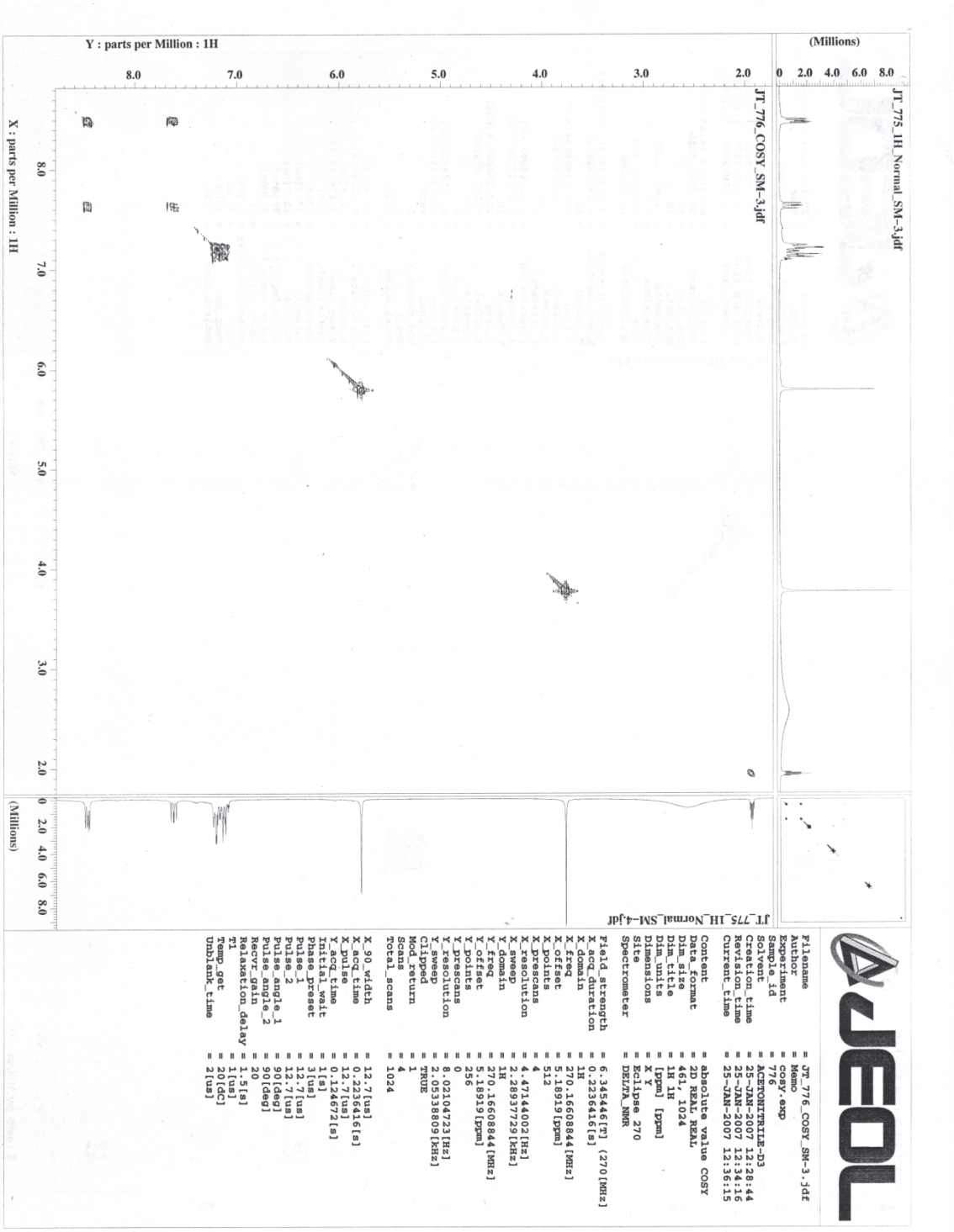

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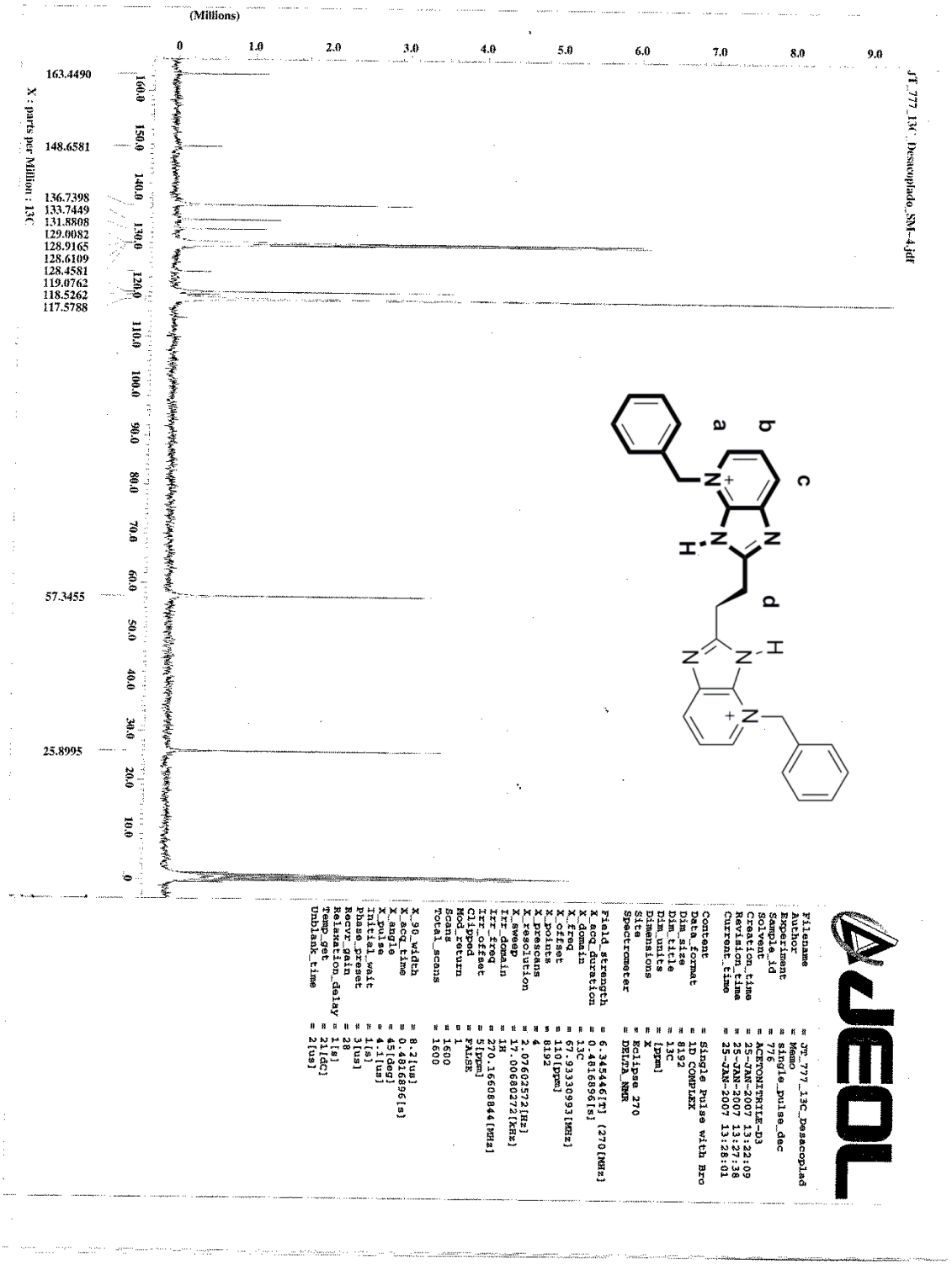
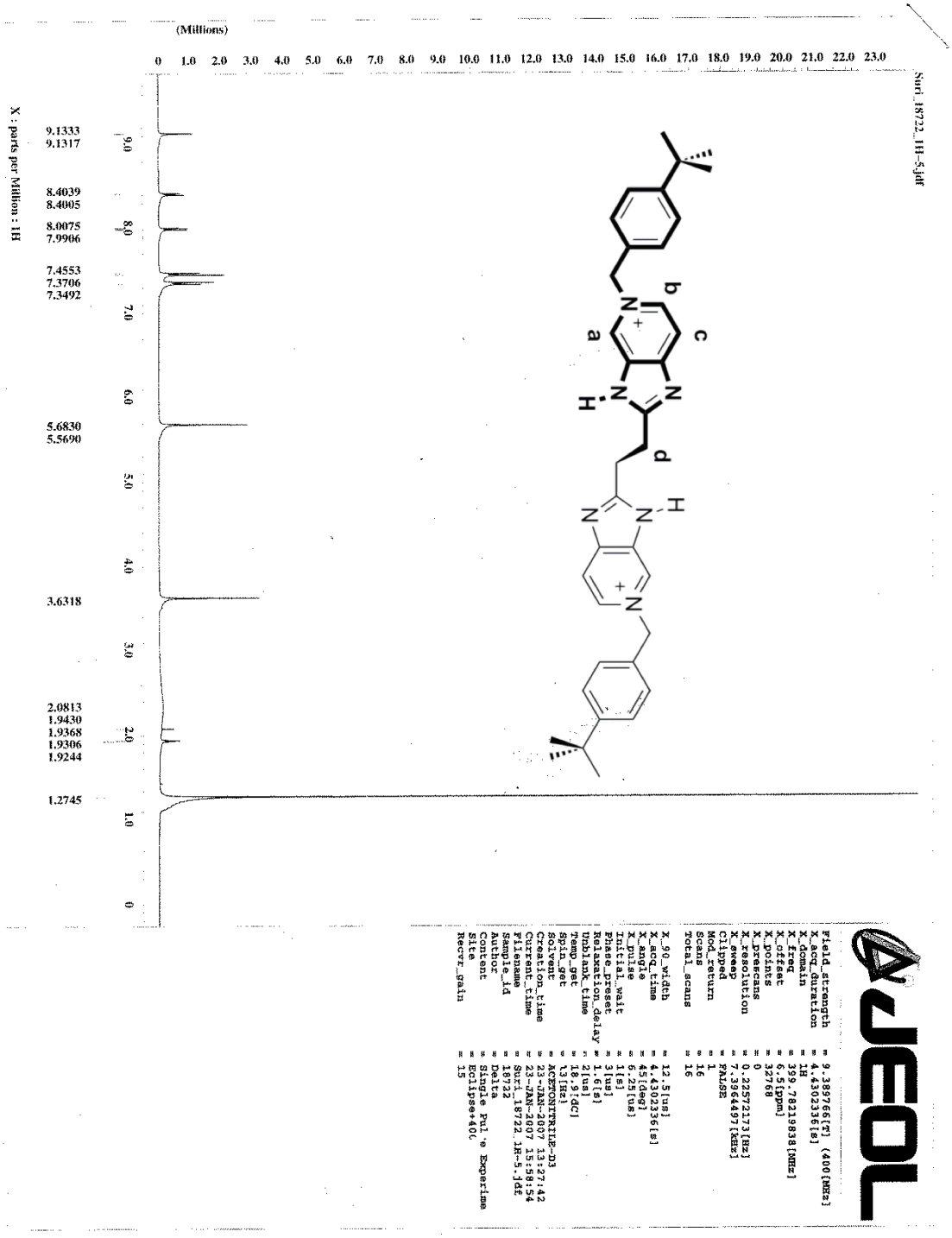
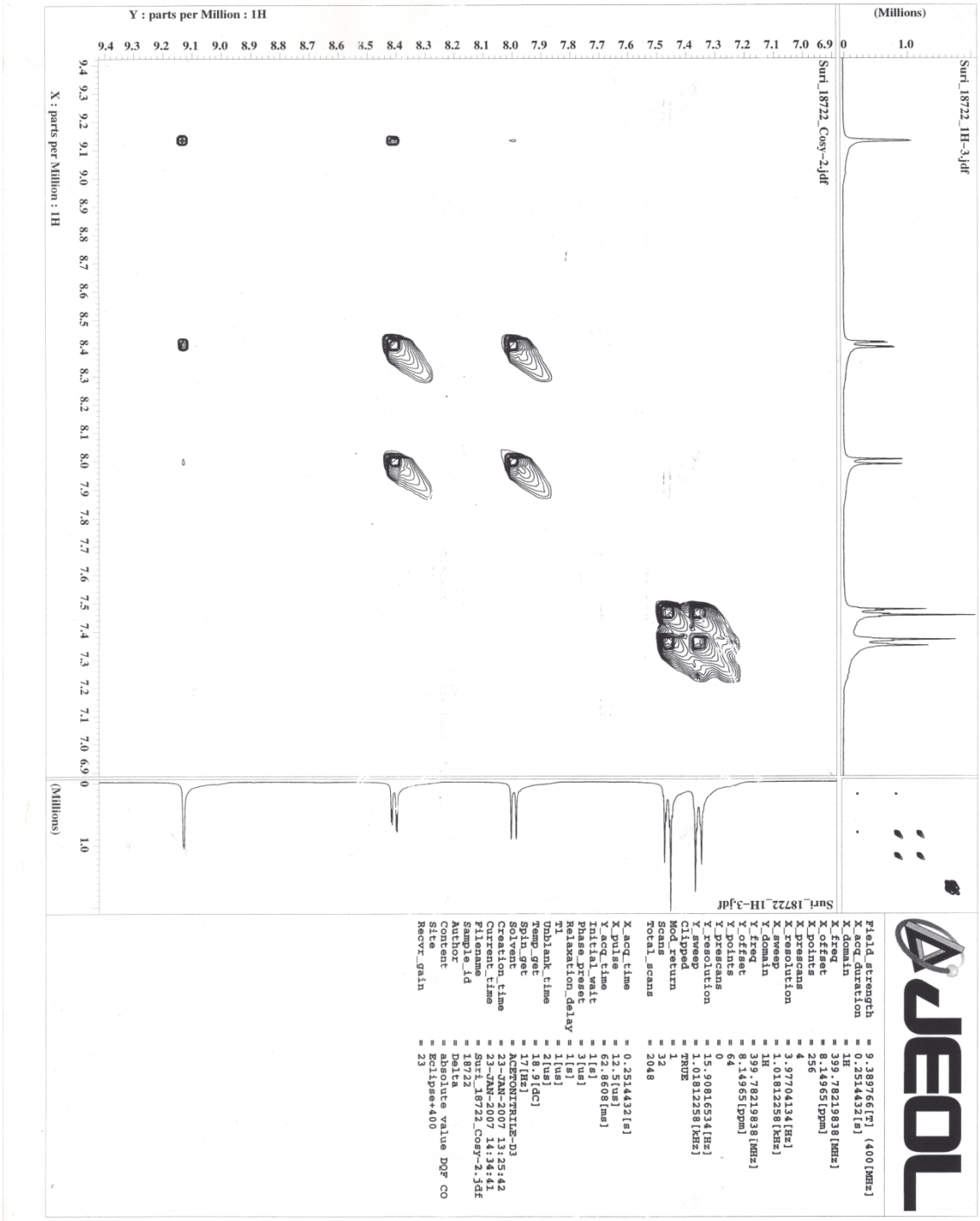


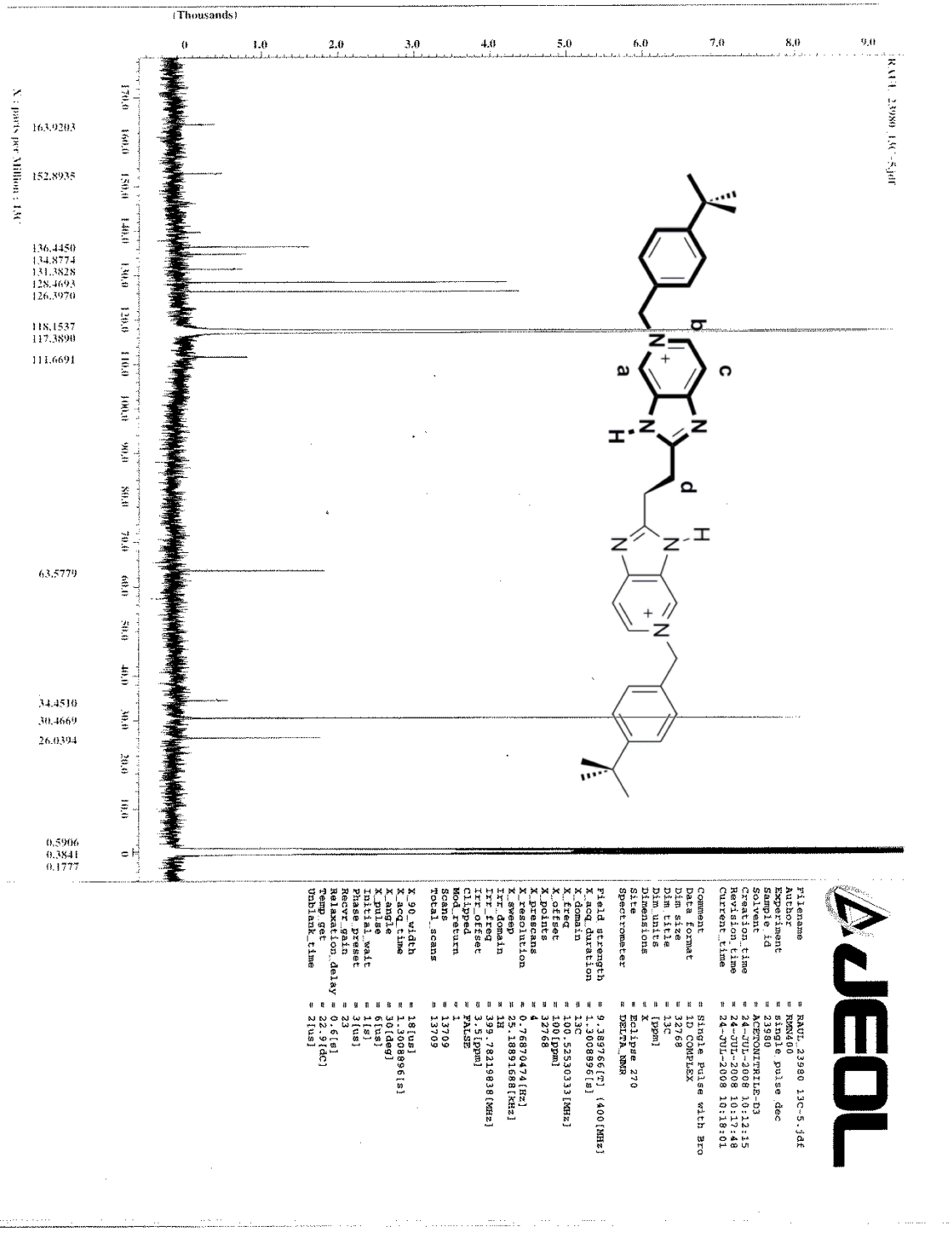
Compound **[2·(*t*BuBn)$_2$][CF$_3$SO$_3$]$_2$** ^{1}H NMR (CD$_3$CN 400 MHz)



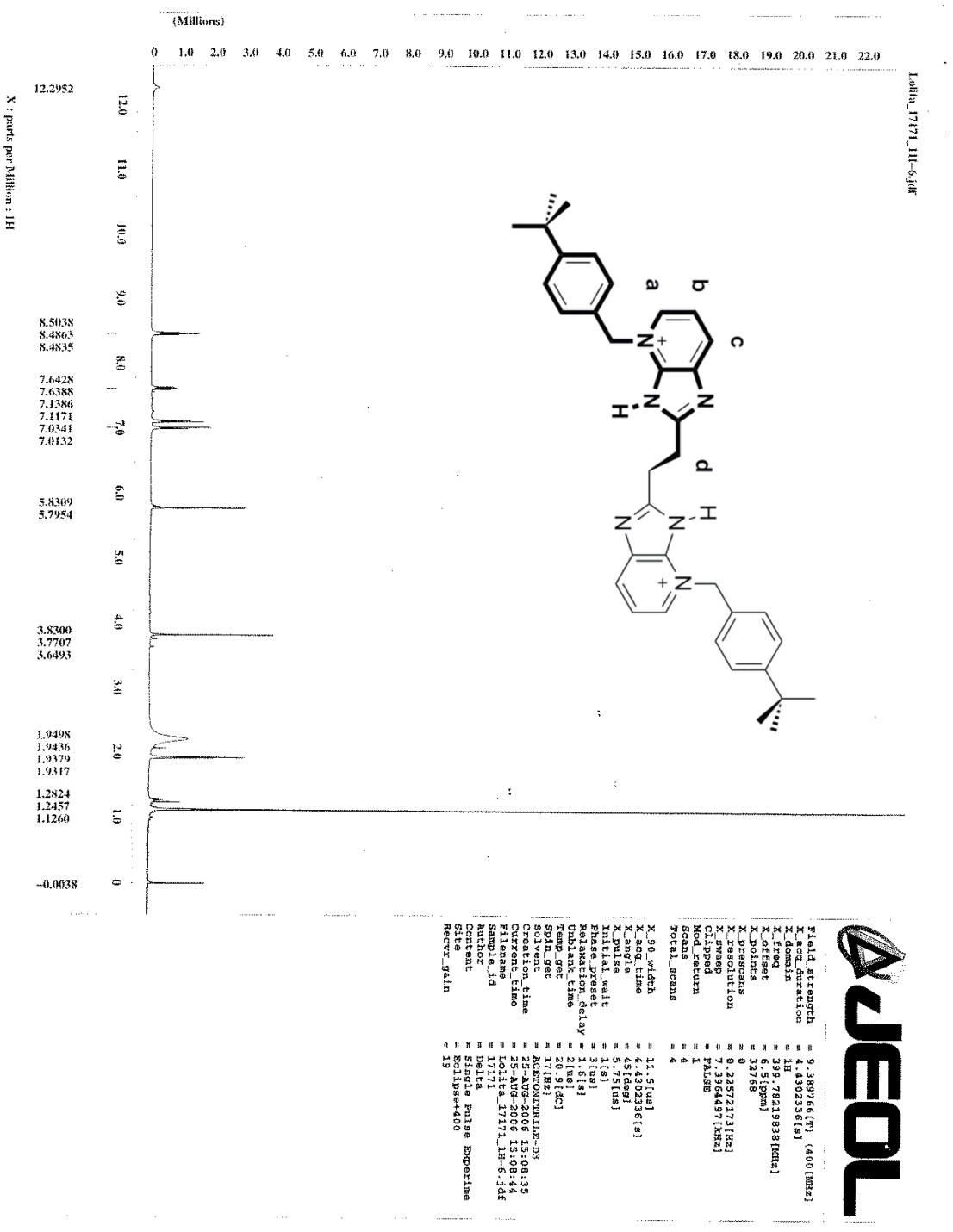
Compound **[2·(*t*BuBn)$_2$][CF$_3$SO$_3$]$_2$** COSY ^{1}H-^{1}H (CD$_3$CN, 400 MHz)



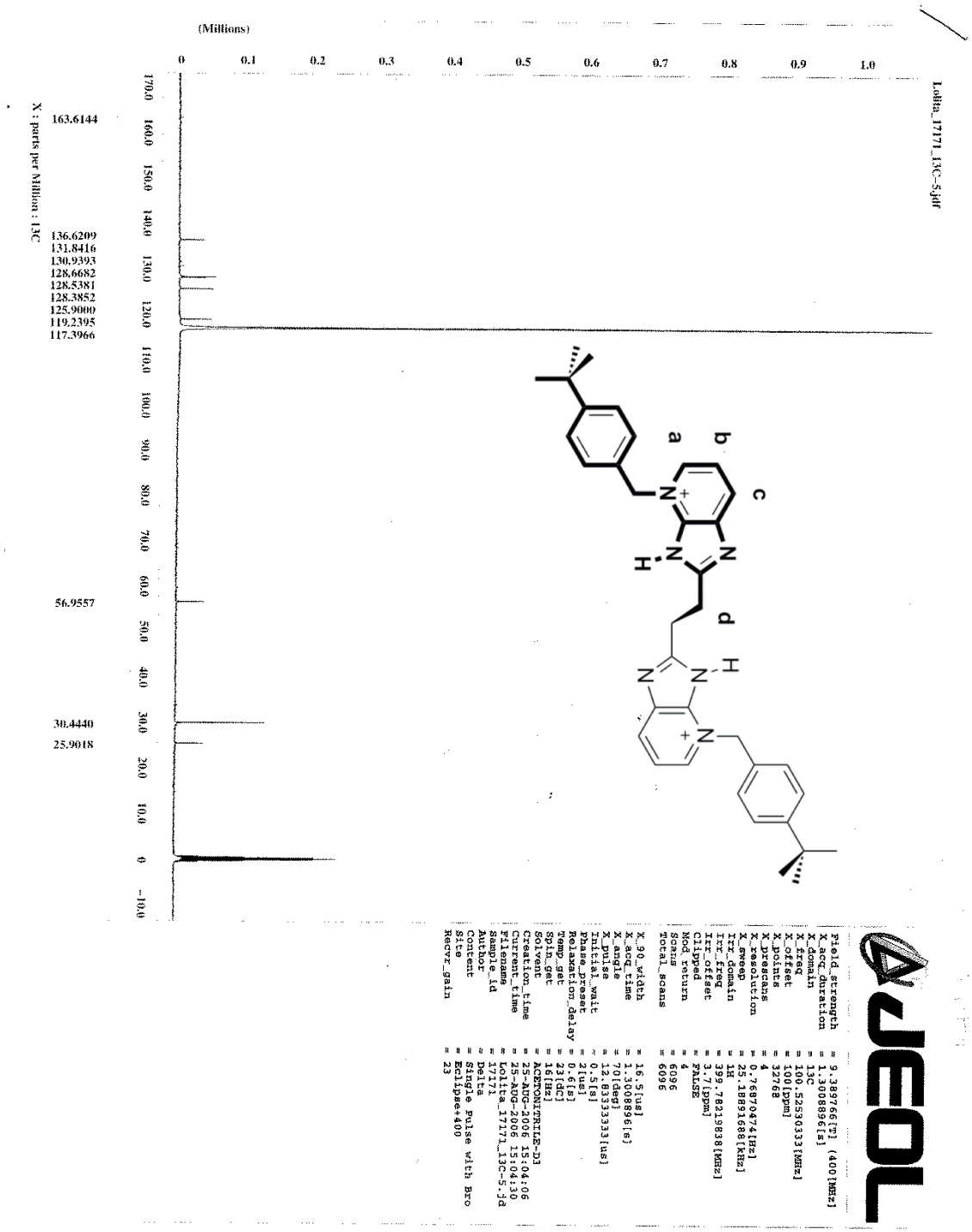
Compound **[2·(*t*BuBn)$_2$][CF$_3$SO$_3$]$_2$** ^{13}C NMR (CD$_3$CN 100 MHz)



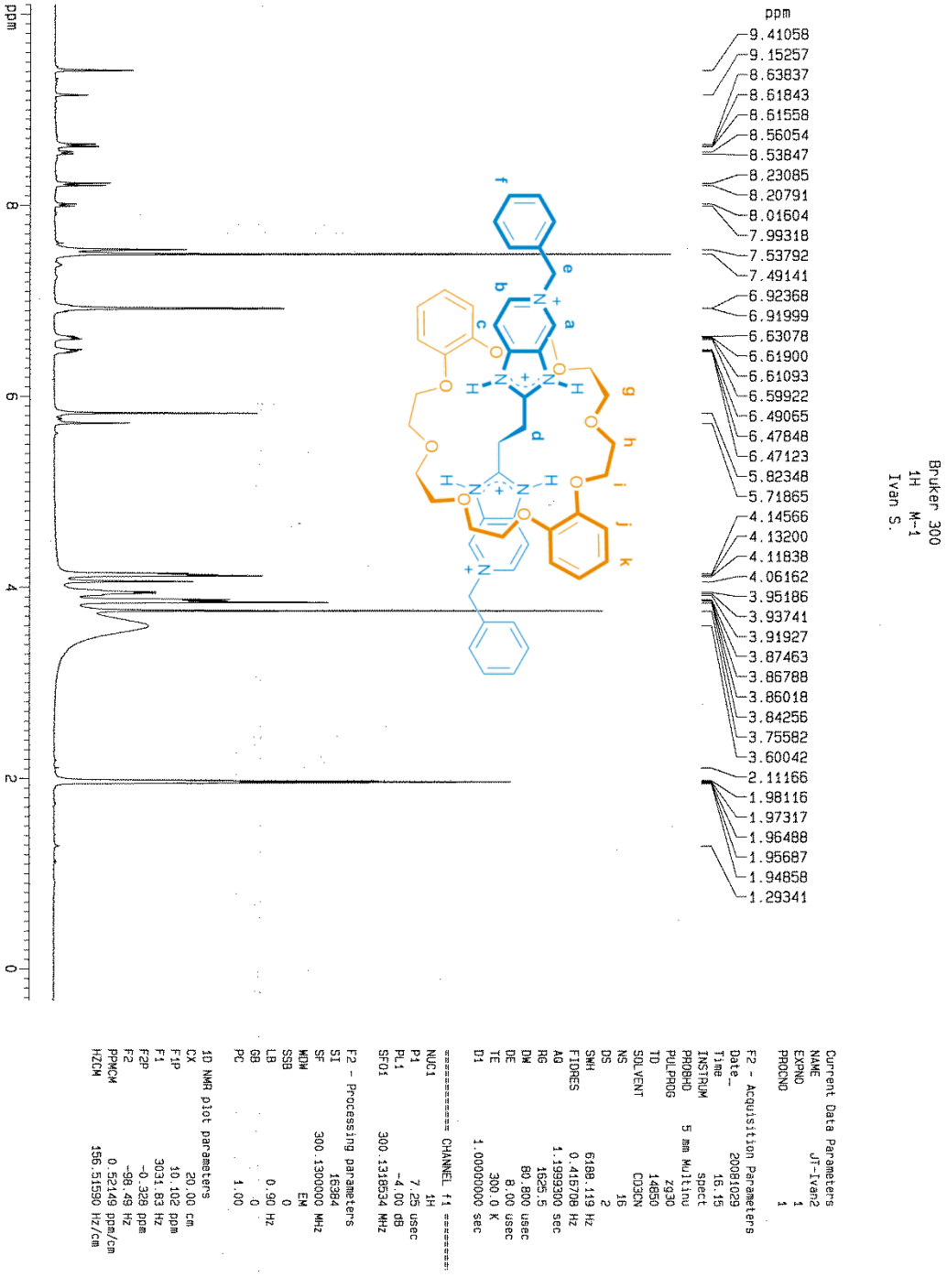
Compound **[3·(*t*BuBn)$_2$][CF$_3$SO$_3$]$_2$** ^{1}H NMR (CD$_3$CN 400 MHz)



Compound **[3·(*t*BuBn)$_2$][CF$_3$SO$_3$]$_2$** ^{13}C NMR (CD$_3$CN 100 MHz)



Compound **{[2•Bn$_2$H$_2$]⊂DB24C8}[CF$_3$SO$_3$]$_4$** ^{1}H NMR (CD$_3$CN 300 MHz)



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PROCNO 1

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Continuous Variation Method for complexation of $[2\cdot H_4][CF_3SO_3]_4$, $[3\cdot H_4][CF_3SO_3]_4$ and $[2\cdot Me_2H_2][CF_3SO_3]_4$ with DB24C8 by ^1H NMR in CD_3CN

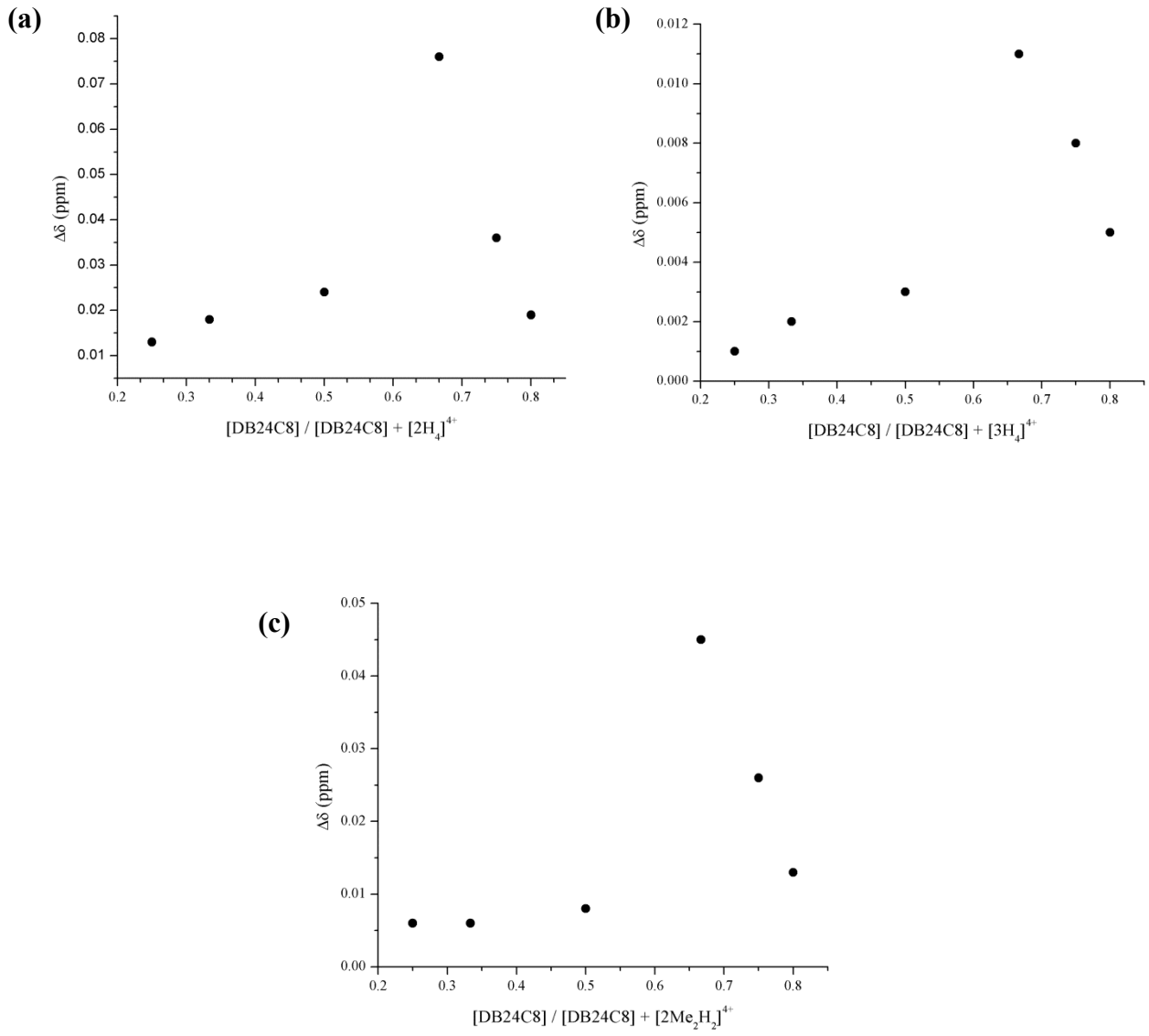

Figure S1. Job´s plots for complexation of **DB24C8** with (a) $[2\cdot H_4]^{4+}$, (b) $[3\cdot H_4]^{4+}$ and (c) $[2\cdot Me_2H_2]^{4+}$.

^{1}H NMR titration between $[2\cdot H_4]^{4+}$, $[3\cdot H_4]^{4+}$ and $[2\cdot Me_2H_2]^{4+}$ with DB24C8 in CD_3CN.

Trifluoromethanesulfonic acid 0.1 M were added to 0.5 mL of 2.0×10^{-3} M solution of compound **$[2\cdot H_2][CF_4SO_3]_2$** in CD_3CN. Twenty aliquots of 2.0×10^{-4} M of **DB24C8** in CD_3CN were consecutively added and individual ^{1}H NMR spectra were recorded on a 300 MHz spectrophotometer at 25 °C. Identical procedures were carried out for compounds **$[3\cdot H_2][CF_4SO_3]_2$** and **$[2\cdot Me_2H_2][CF_4SO_3]_2$.** Chemical shifts for protons H_b of the three axles were submitted to a least-square fitting analysis with the software WinEQNMR2[1] previous correction for dilution bias and the corresponding association constants were determined.

Experimental and fitting calculations are shown in Figure S2.

(1) Hynes, M. J. *J. Chem. Soc., Dalton Trans.* **1993**, 311.

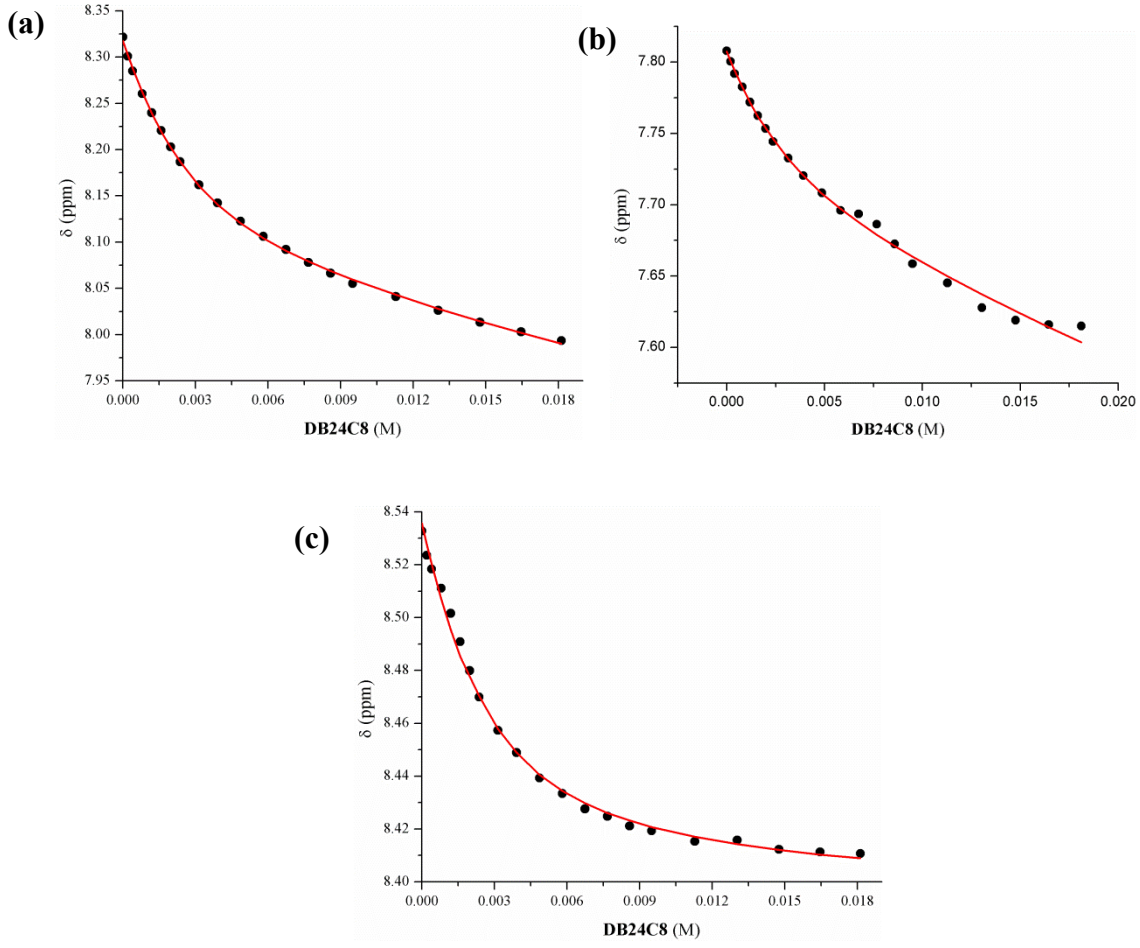

Figure S2. Chemical shifts of aromatic H_b proton of compounds (a) **$[2\cdot H_2][CF_4SO_3]_2$**, (b) **$[3\cdot H_2][CF_4SO_3]_2$** and (c) **$[2\cdot Me_2H_2][CF_4SO_3]_2$** in the titration with **DB24C8** in acetonitrile-d_3.

NOESY of compound {[2·Me_2H_2]⊂DB24C8}[CF_3SO_3]$_4$

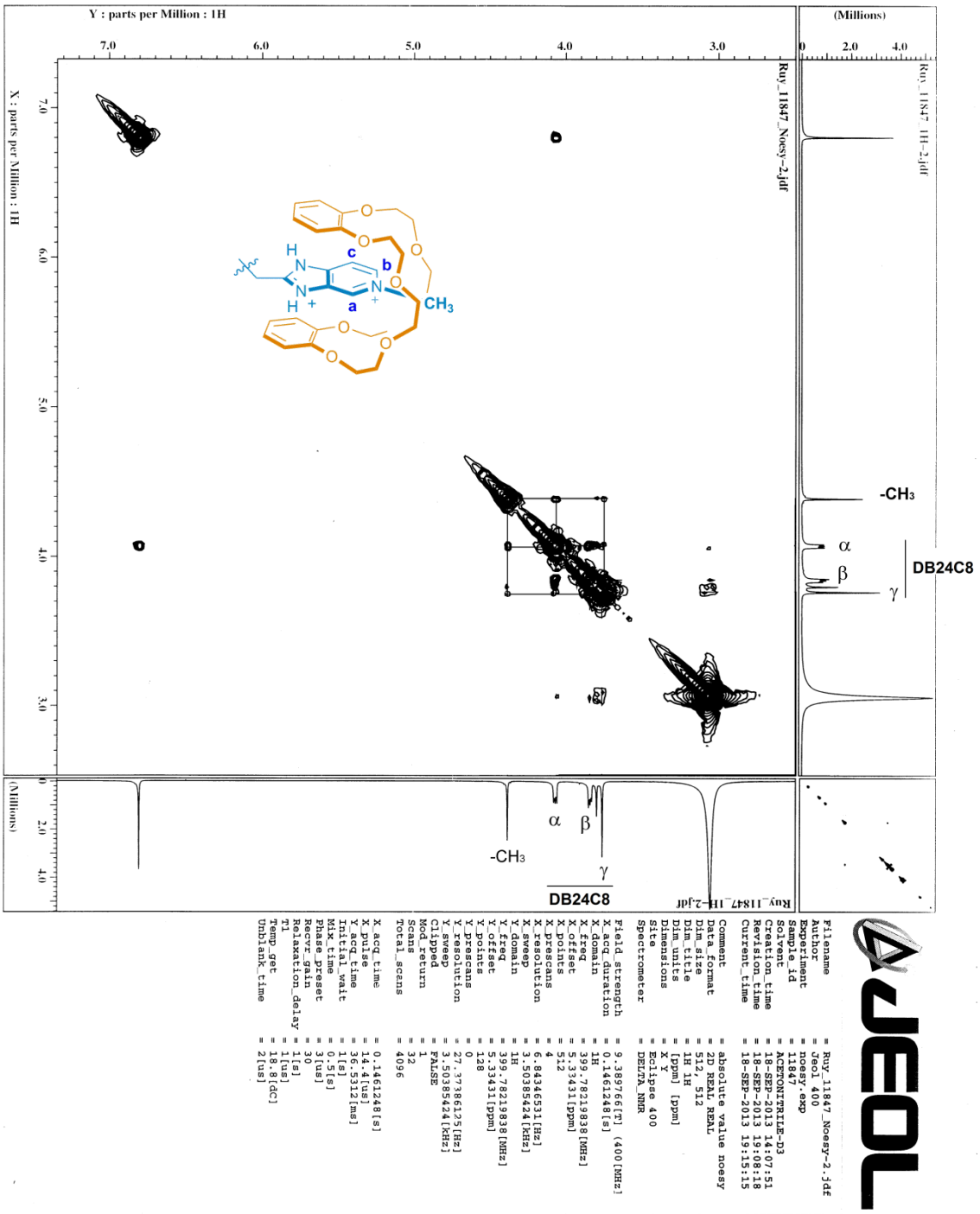

Figure S3. NOESY of {[2·Me_2H_2]·DB24C8}[CF_3SO_3]$_4$ (CD_3CN, 400 MHz).

Details of Crystal Structure Determination for compounds $[2\cdot Bn_2][CF_3SO_3]_2\cdot H_2O$, $[3\cdot Bn_2]Br_2\cdot CHCl_3$ and $\{[2\cdot Bn_2H_2]\subset DB24C8\}[CF_3SO_3]_4$

Crystals were grown by slow evaporation of: i) saturated aqueous solution of axle $[\mathbf{2}\cdot Bn_2][CF_3SO_3]_2$, ii) axle $[\mathbf{3}\cdot Bn_2]Br_2$ in an $CH_3CN/CHCl_3$ solvent mixture and iii) saturated solution containing $[\mathbf{2}\cdot Bn_2H_2][CF_3SO_3]_4$ and three equivalents of **DB24C8** in CH_3CN. Crystals were mounted on a glass fibre. A full hemisphere of data were collected with 30s frames on a Enraf-Nonius Kappa diffractometer fitted with a CCD based detector using MoK_α radiation (0.71073 Å). Diffraction data and unit-cell parameters were consistent with the assigned space groups. The structures were solved by direct methods, completed by subsequent Fourier syntheses and refined with full-matrix least-squares methods against $|F^2|$ data. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were treated as idealized contributions.

Table 1. Crystallographic data, solution and refinement parameters for single crystal structure determinations of compounds **$[2\cdot Bn_2][CF_3SO_3]_2\cdot H_2O$**, **$[3\cdot Bn_2]Br_2\cdot CHCl_3$** and **$\{[2\cdot Bn_2H_2]\subset DB24C8\}[CF_3SO_3]_4$**.

	$[2\cdot Bn_2][CF_3SO_3]_2\cdot H_2O$	$[3\cdot Bn_2]Br_2\cdot CHCl_3$	$\{[2\cdot Bn_2H_2]\subset DB24C8\}[CF_3SO_3]_4$
Formula	$C_{30}H_{30}F_6N_6O_8S_2$	$C_{29}H_{27}Cl_3\ Br_2N_6$	$C_{56}H_{60}F_{12}N_6O_{20}S_4$
formula weight	780.72	725.74	1493.34
crystal system	monoclinic	monoclinic	monoclinic
space group	*P*21/c	*P*21/n	*P*21/n
T (K)	293(2)	293(2)	293(2)
a [Å]	11.281(2)	9.925(1)	12.368(3)
b [Å]	8.829(2)	12.232(1)	10.385(2)
c [Å]	17.148(3)	25.401(1)	25.353(5)
α [°]			
β [°]	95.77(3)	97.864(1)	90.87(3)
γ [°]			
V [Å^3]	1699.4(6)	3054.7(5)	3256.3(1)
Z	2	4	2
D_{calc} [g/cm^3]	1.526	1.578	1.523
μ (mm^{-1})	0.249	2.946	0.258
reflections collected	14084	13014	24319
unique reflections	3622	5507	5705
R_1/R_2w [$I > 2\sigma(I)$][a]	0.1207/0.2045	0.0746/0.1652	0.0939/0.2417
R_1/R_2w (all data)	0.2030/0.2448	0.1652/0.2026	0.1949/0.2958
GoF on F^2	1.194	1.031	1.058
Parameters/restrains	243/0	361/0	442/0
Min/max residual density [e/Å^3]	0.32/-0.28	0.77 /-0.79	0.59/-0.34

[a] $R_1 = \Sigma||F_o| - |F_c||\Sigma\ |F_o|$;
[b] $R_2w = [\Sigma\ [w(F_o^2 - F_c^2)^2] / \Sigma\ [w(F_o^2)^2]]^{1/2}$, where $w = q[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.

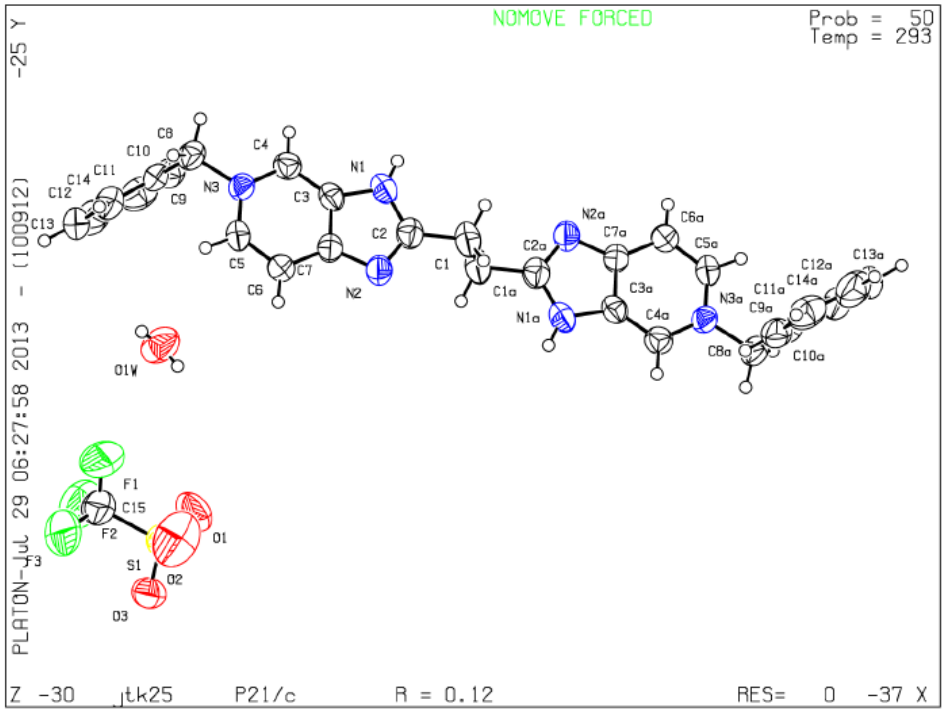

Figure S4. ORTEP representation of compound **[2·Bn$_2$][CF$_3$SO$_3$]$_2$·H$_2$O**.

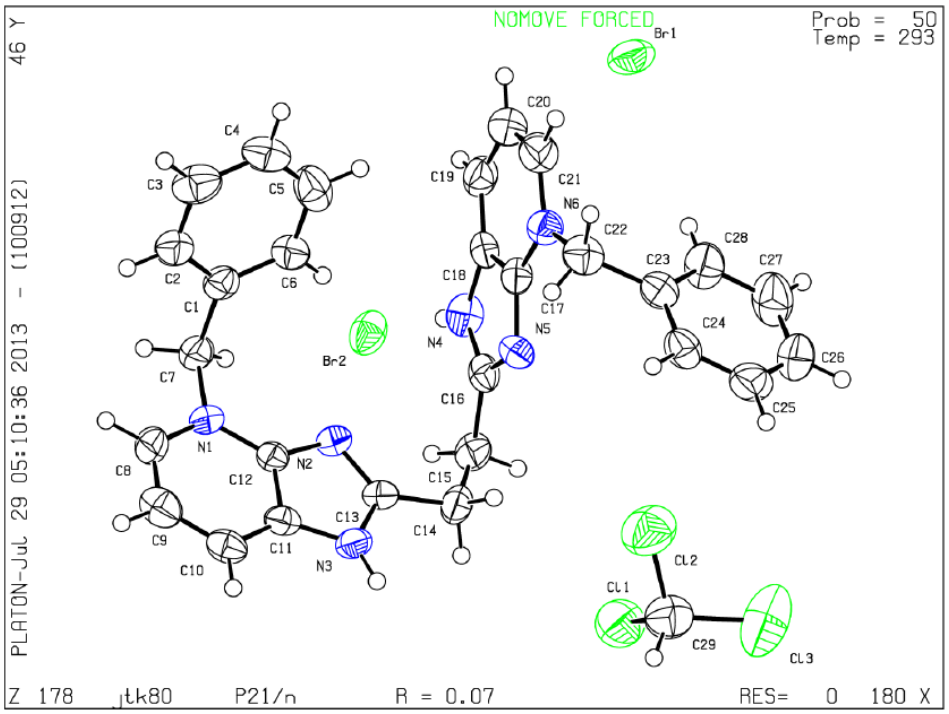

Figure S5. ORTEP representation of compound **[3·Bn$_2$]Br$_2$·CHCl$_3$**.

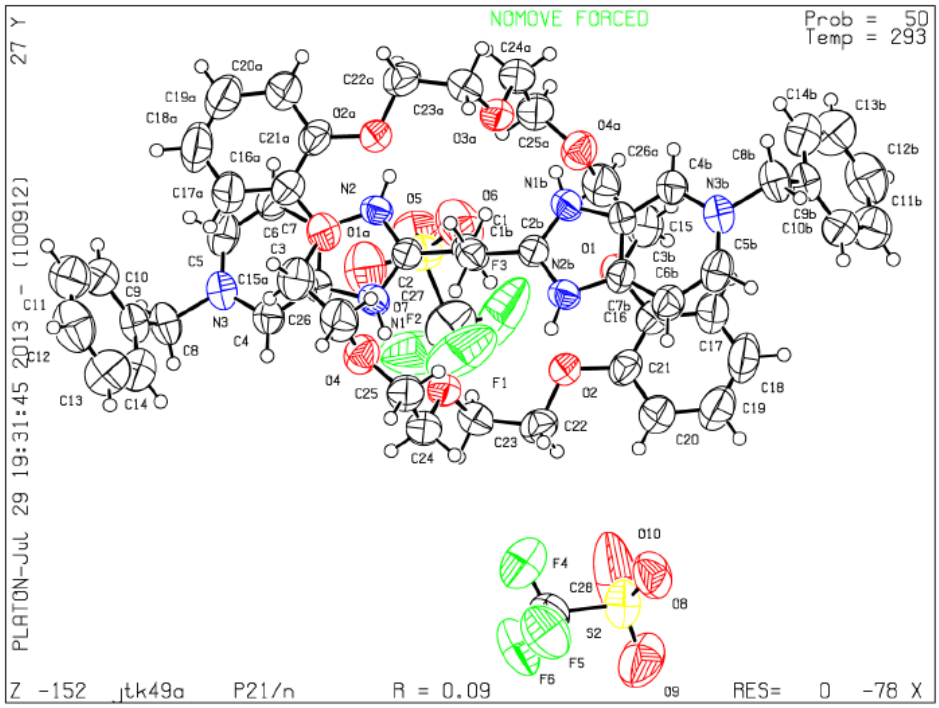

Figure S6. ORTEP representation of compound **{[2·Bn$_2$H$_2$]⊂DB24C8}[CF$_3$SO$_3$]$_4$**.