

Supplementary Material

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

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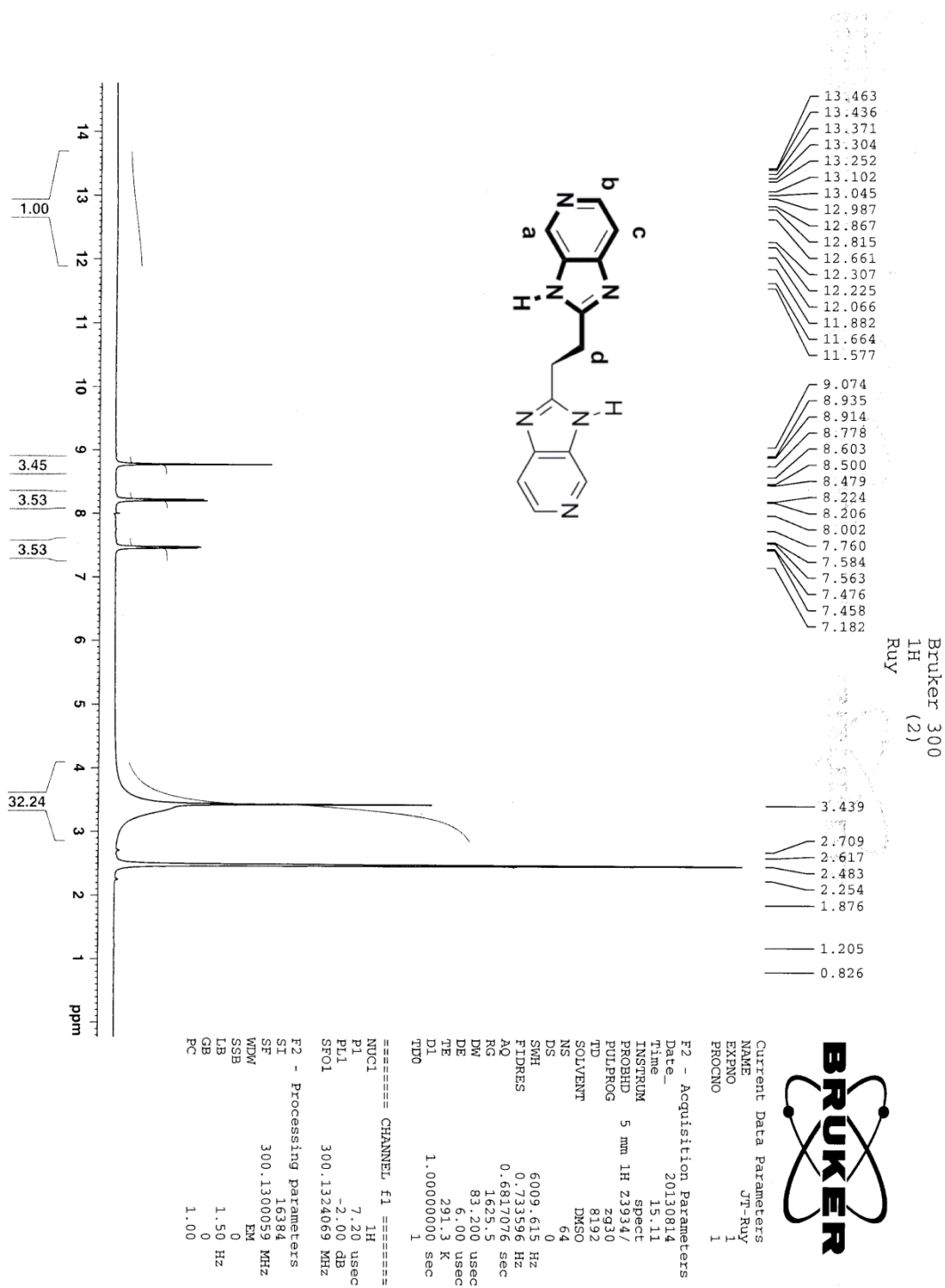
jtiburcio@cinvestav.mx

Table of Contents

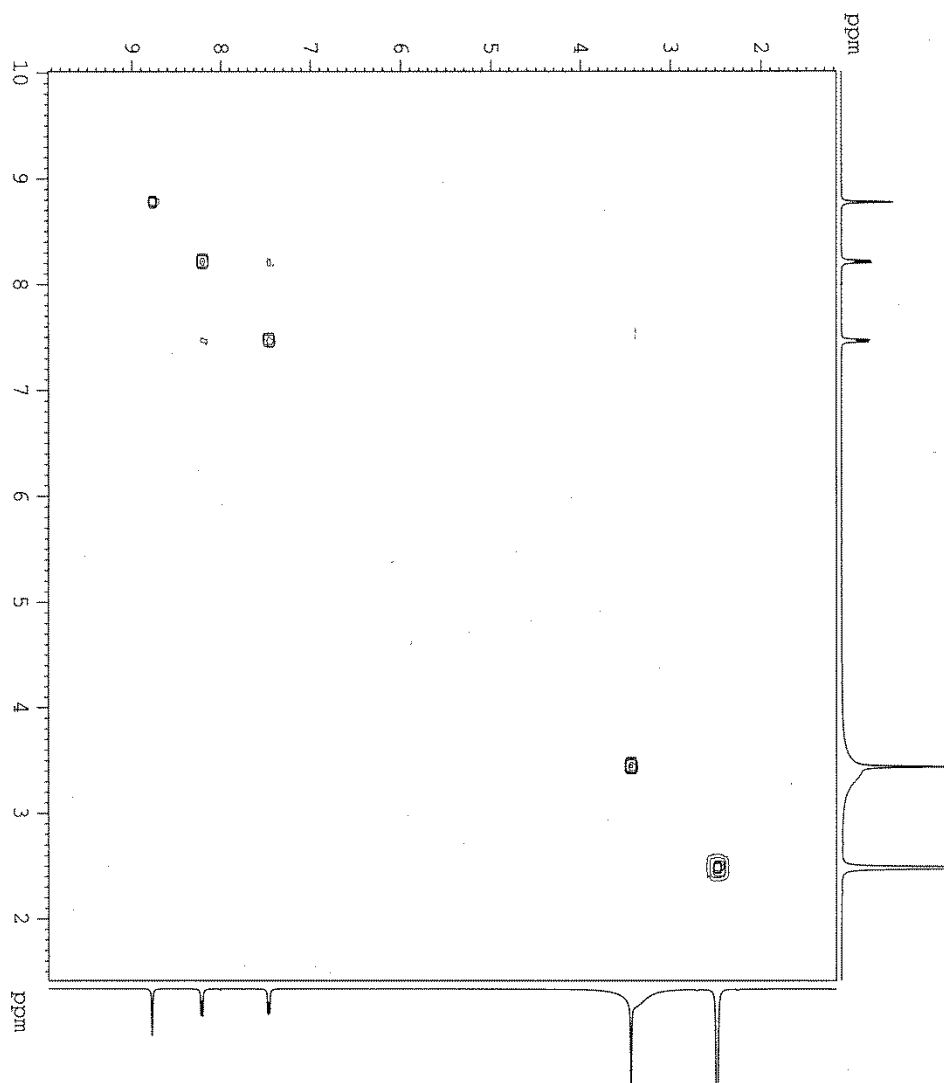
^1H and ^{13}C NMR	S4–S27
Compound [2]	
^1H NMR (DMSO- d_6 , 300 MHz)	S4
COSY ^1H - ^1H (DMSO- d_6 , 300 MHz)	S5
^{13}C NMR (DMSO- d_6 , 68 MHz)	S6
Compound [3]	
^1H NMR (DMSO- d_6 , 300 MHz)	S7
COSY ^1H - ^1H (DMSO- d_6 , 270 MHz)	S8
^{13}C NMR (DMSO- d_6 , 68 MHz)	S9
Compound [2·Me ₂][CF ₃ SO ₃] ₂	
^1H NMR (CD ₃ CN, 400 MHz)	S10
COSY ^1H - ^1H (CD ₃ CN, 270 MHz)	S11
^{13}C NMR (CD ₃ CN, 100 MHz)	S12
Compound [3·Me ₂][CF ₃ SO ₃] ₂	
^1H NMR (CD ₃ CN, 270 MHz)	S13
COSY ^1H - ^1H (CD ₃ CN, 400 MHz)	S14
^{13}C NMR (CD ₃ CN, 68 MHz)	S15
Compound [2·Bn ₂][CF ₃ SO ₃] ₂	
^1H NMR (CD ₃ CN 270 MHz)	S16
COSY ^1H - ^1H (CD ₃ CN, 400 MHz)	S17
^{13}C NMR (CD ₃ CN, 68 MHz)	S18
Compound [3·Bn ₂][CF ₃ SO ₃] ₂	
^1H NMR (CD ₃ CN 400 MHz)	S19

COSY ^1H - ^1H (CD_3CN , 270 MHz)	S20
^{13}C NMR (CD_3CN , 68 MHz)	S21
Compound $[\mathbf{2} \cdot (t\text{BuBn})_2][\text{CF}_3\text{SO}_3]_2$	
^1H NMR (CD_3CN 400 MHz)	S22
COSY ^1H - ^1H (CD_3CN , 400 MHz)	S23
^{13}C NMR (CD_3CN 100 MHz)	S24
Compound $[\mathbf{3} \cdot (t\text{BuBn})_2][\text{CF}_3\text{SO}_3]_2$	
^1H NMR (CD_3CN 400 MHz)	S25
^{13}C NMR (CD_3CN 100 MHz)	S26
Compound $\{[\mathbf{2} \cdot \text{Bn}_2\text{H}_2] \subset \text{DB24C8}\}[\text{CF}_3\text{SO}_3]_4$	
^1H NMR (CD_3CN 300 MHz)	S27
Continuous Variation Method for complexation of $[\mathbf{2} \cdot \text{H}_4][\text{CF}_3\text{SO}_3]_4$, $[\mathbf{3} \cdot \text{H}_4][\text{CF}_3\text{SO}_3]_4$ and $[\mathbf{2} \cdot \text{Me}_2\text{H}_2][\text{CF}_3\text{SO}_3]_4$ with DB24C8 by ^1H NMR in CD_3CN	S28
^1H NMR titration between $[\mathbf{2} \cdot \text{H}_4][\text{CF}_3\text{SO}_3]_4$, $[\mathbf{3} \cdot \text{H}_4][\text{CF}_3\text{SO}_3]_4$ and $[\mathbf{2} \cdot \text{Me}_2\text{H}_2][\text{CF}_3\text{SO}_3]_4$ with DB24C8 in CD_3CN	S29
NOESY of compound $\{[\mathbf{2} \cdot \text{Me}_2\text{H}_2] \cdot \text{DB24C8}\}[\text{CF}_3\text{SO}_3]_4$	S30
Details of Crystal Structure Determination for compounds $[\mathbf{2} \cdot \text{Bn}_2][\text{CF}_3\text{SO}_3]_2 \cdot \text{H}_2\text{O}$, $[\mathbf{3} \cdot \text{Bn}_2]\text{Br}_2 \cdot \text{CHCl}_3$ and $\{[\mathbf{2} \cdot \text{Bn}_2\text{H}_2] \subset \text{DB24C8}\}[\text{CF}_3\text{SO}_3]_4$	S31–S33

Compound [2] ¹H NMR (DMSO-d₆, 300 MHz)

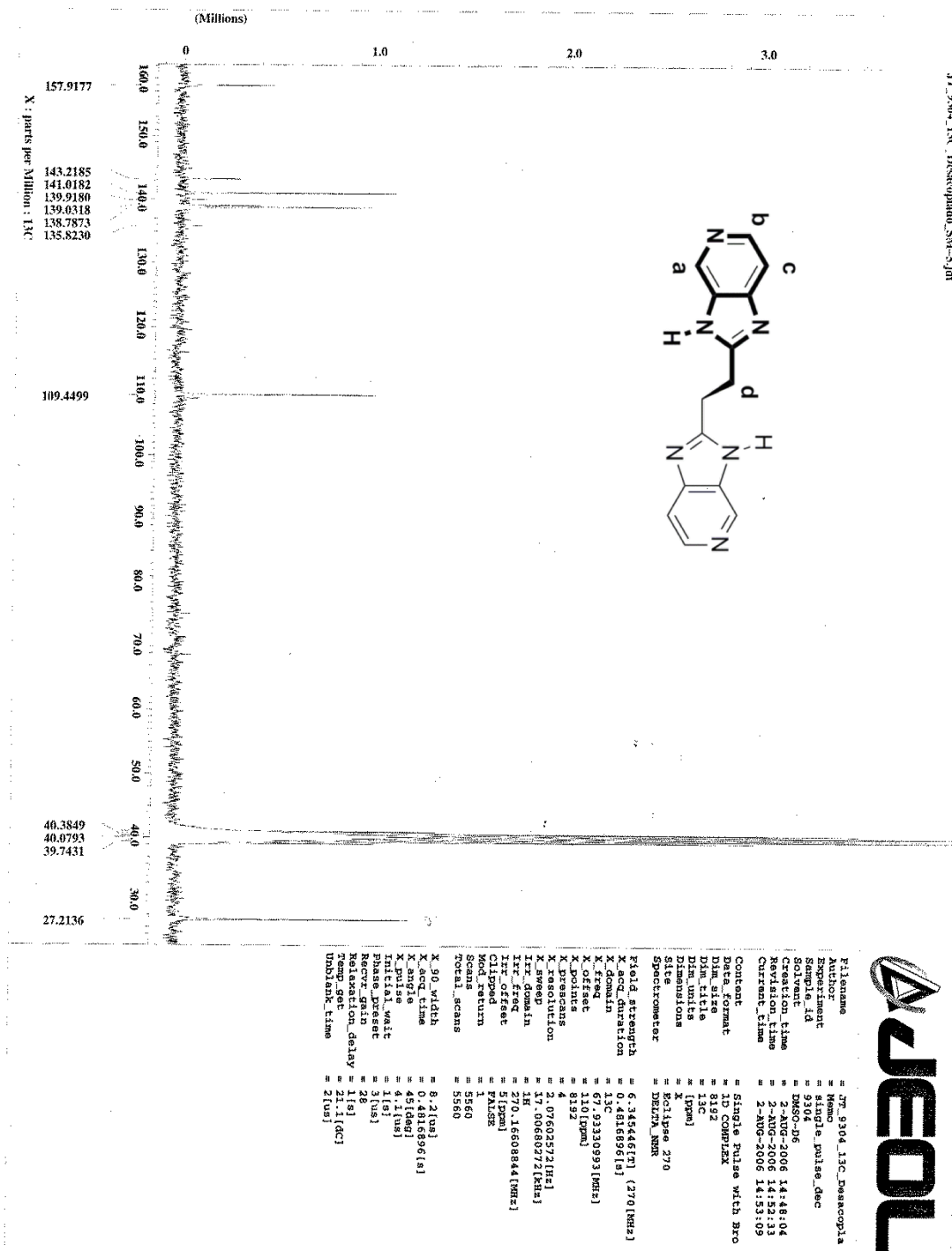


Bruker 300
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 Ruy

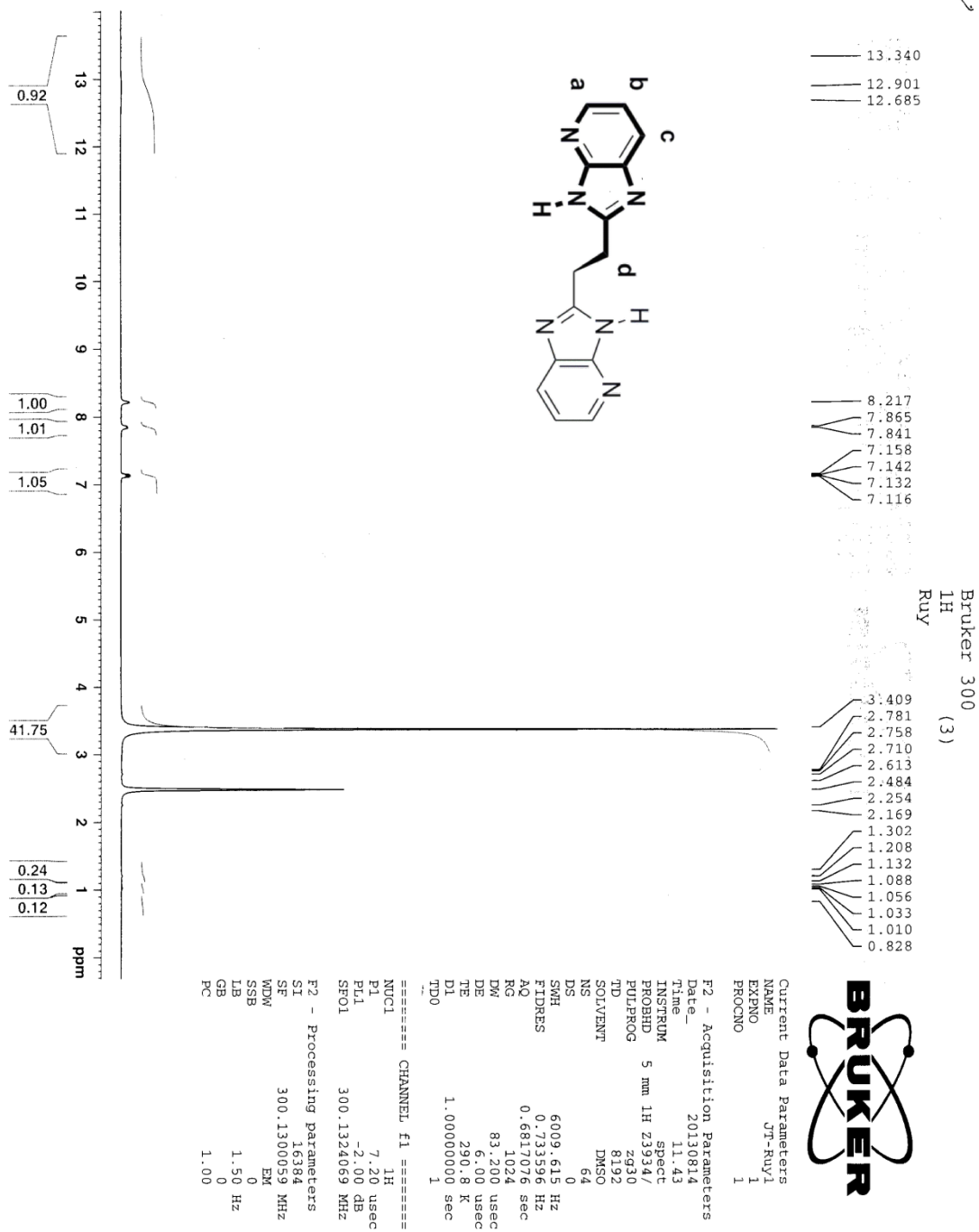


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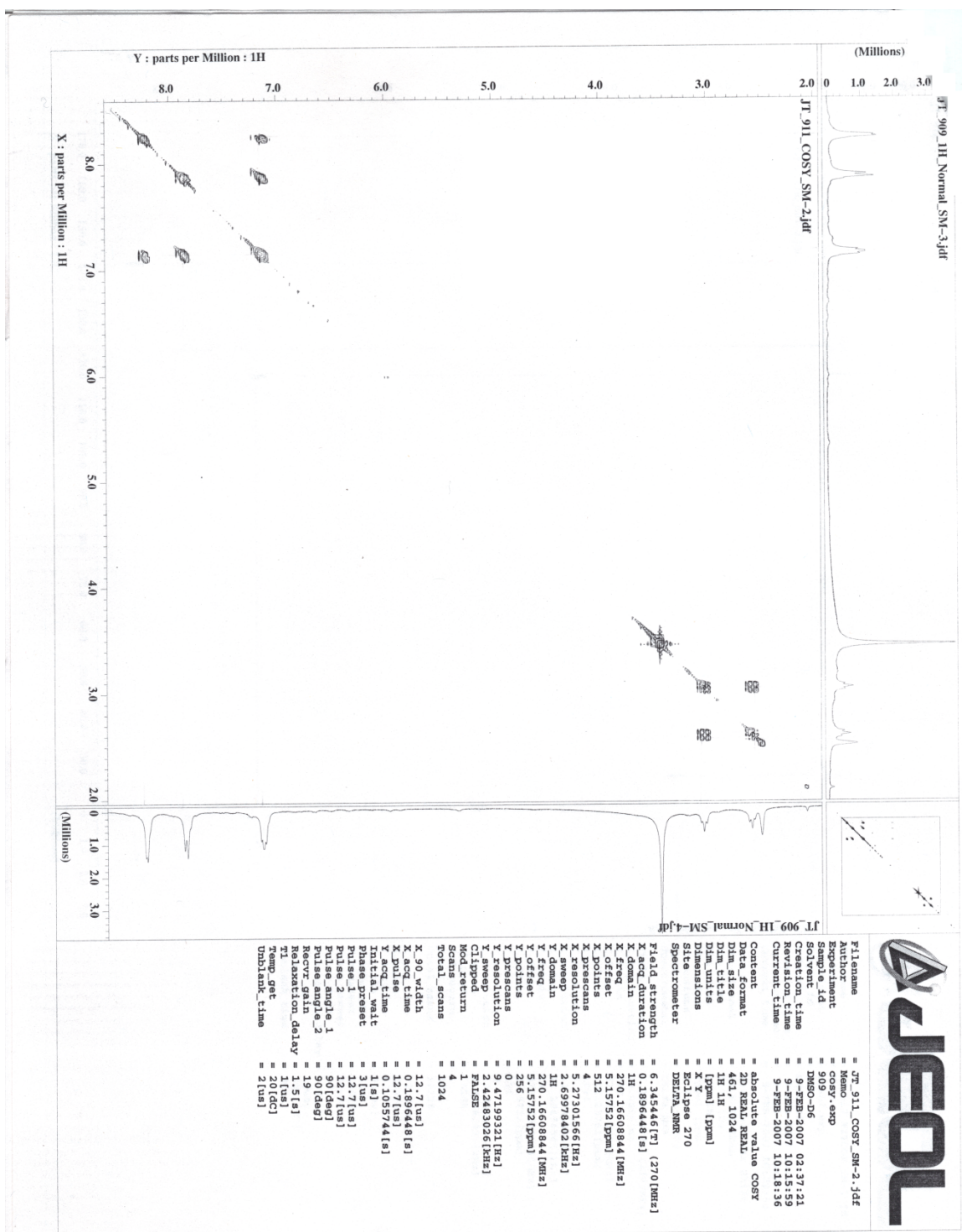
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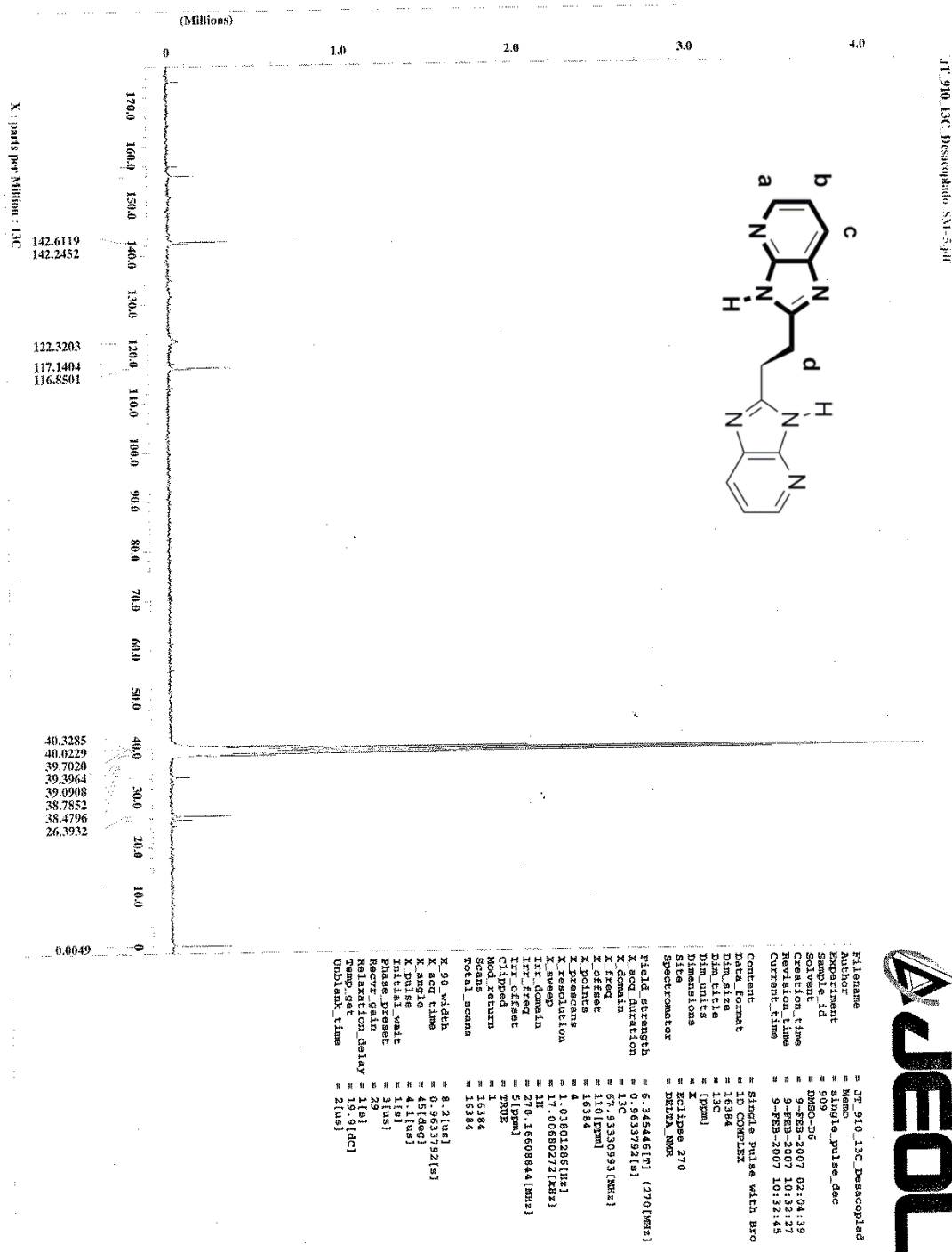
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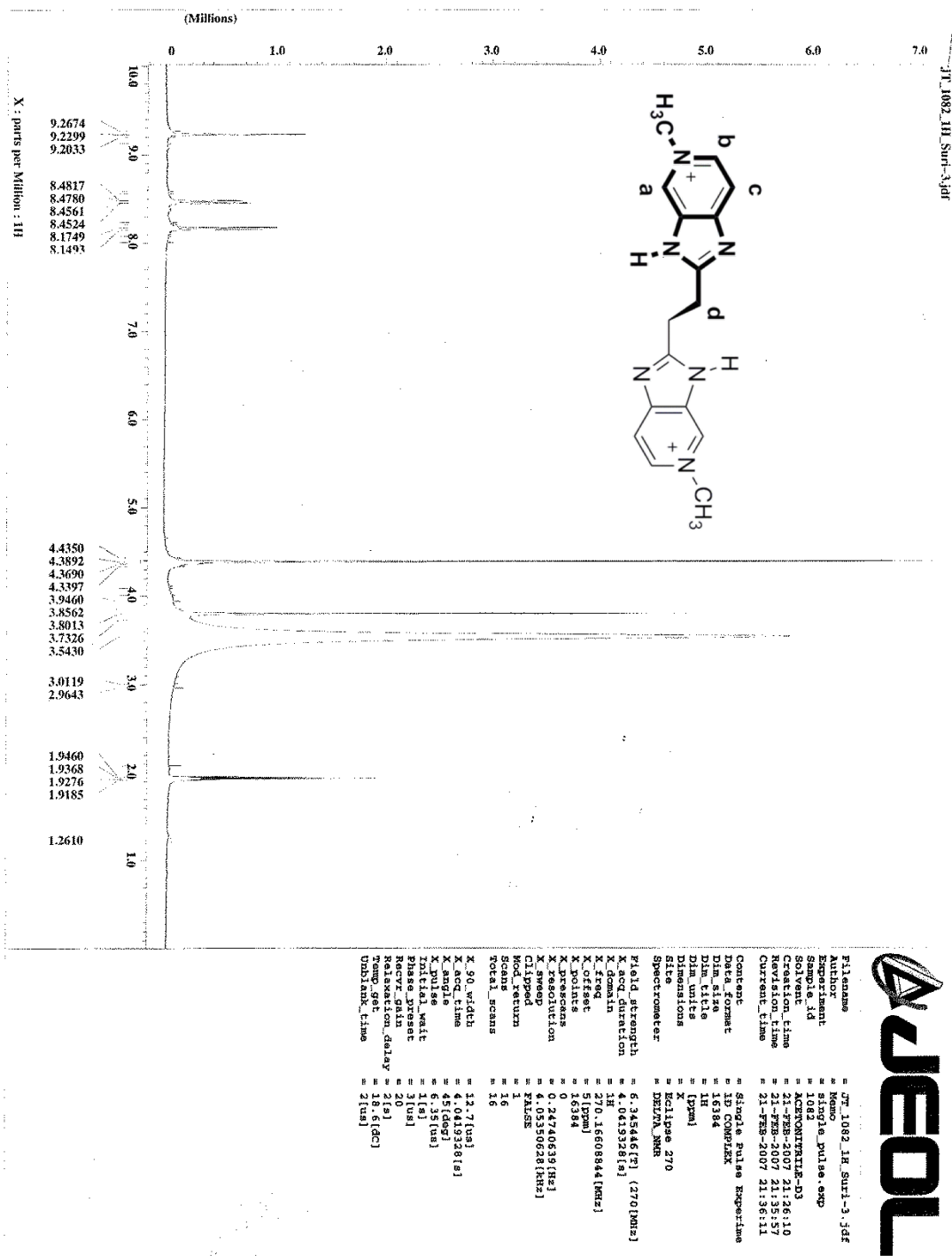
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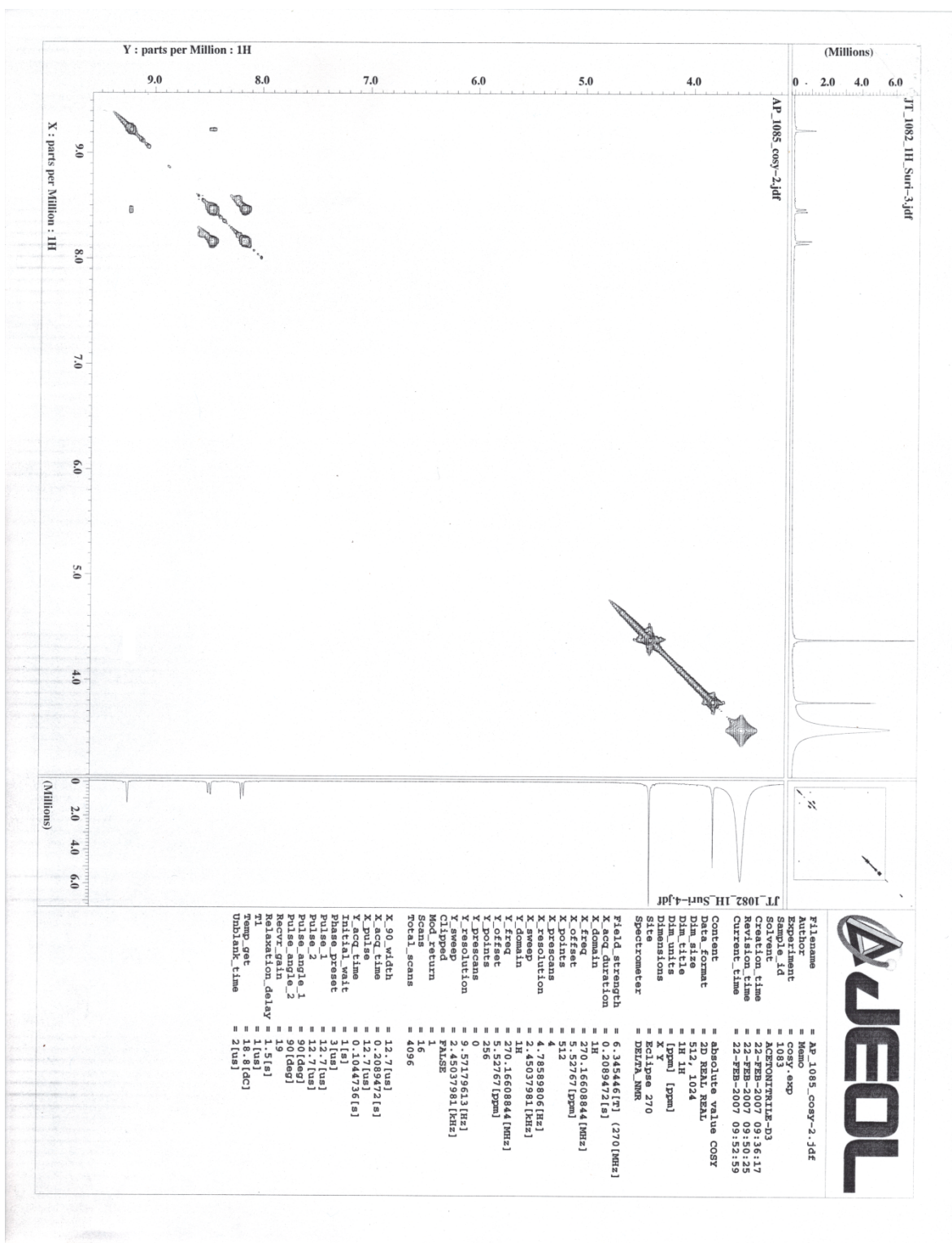
Compound [3] ^{13}C NMR (DMSO- d_6 , 68 MHz)



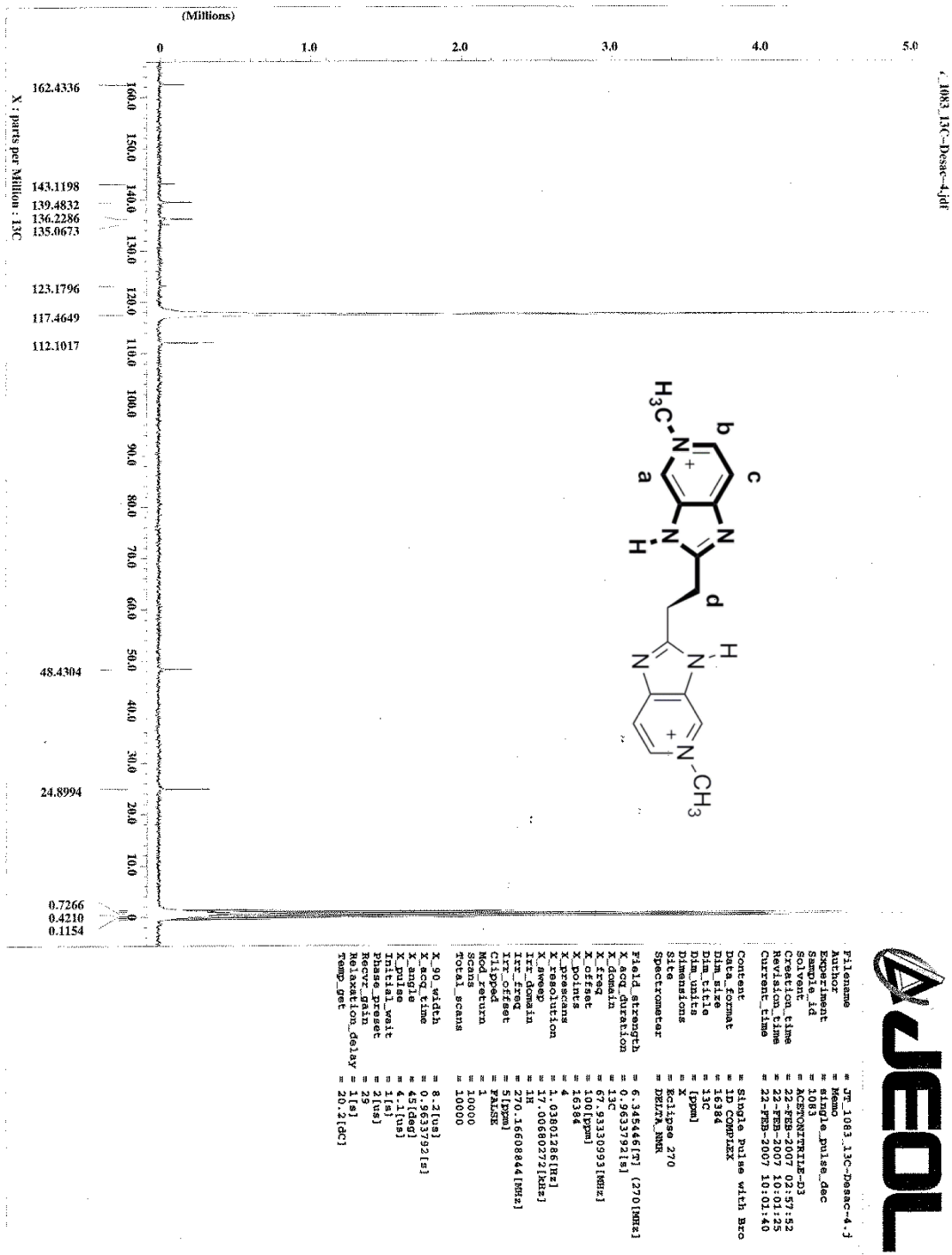
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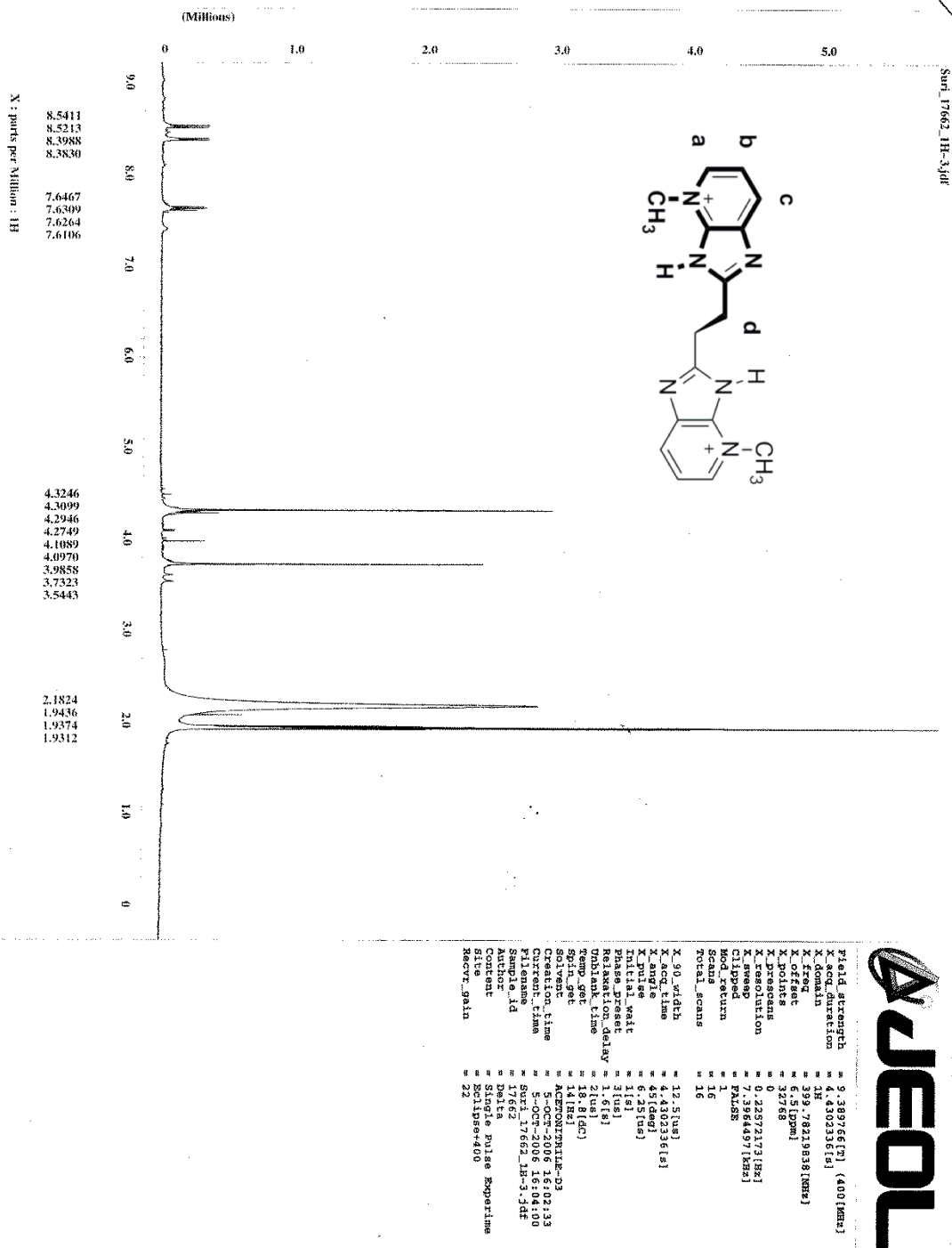
Compound $[2 \cdot \text{Me}_2][\text{CF}_3\text{SO}_3]_2$ COSY ^1H - ^1H NMR (CD_3CN , 270 MHz)



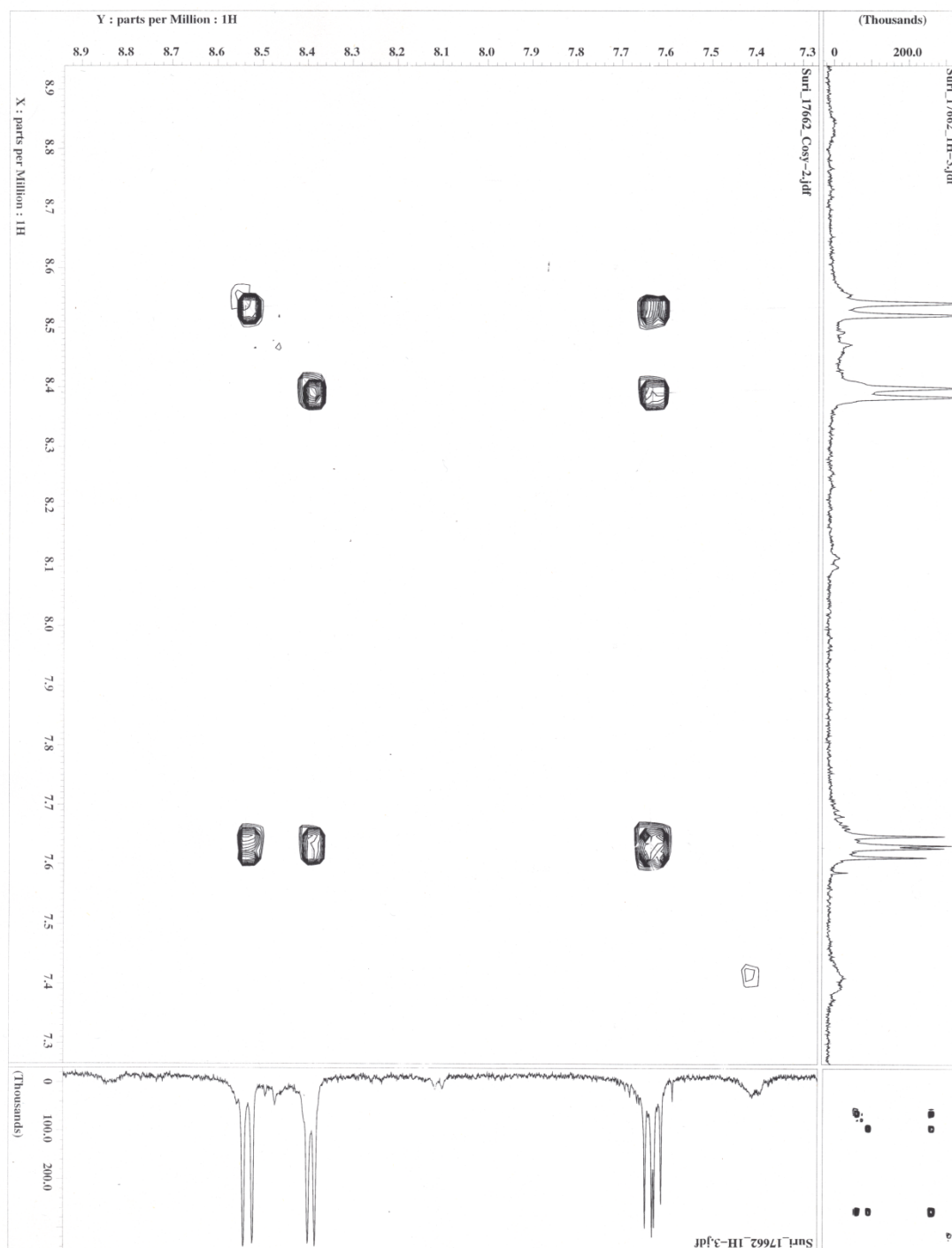
Compound **[2·Me₂][CF₃SO₃]₂** ¹³C NMR (CD₃CN, 68 MHz)



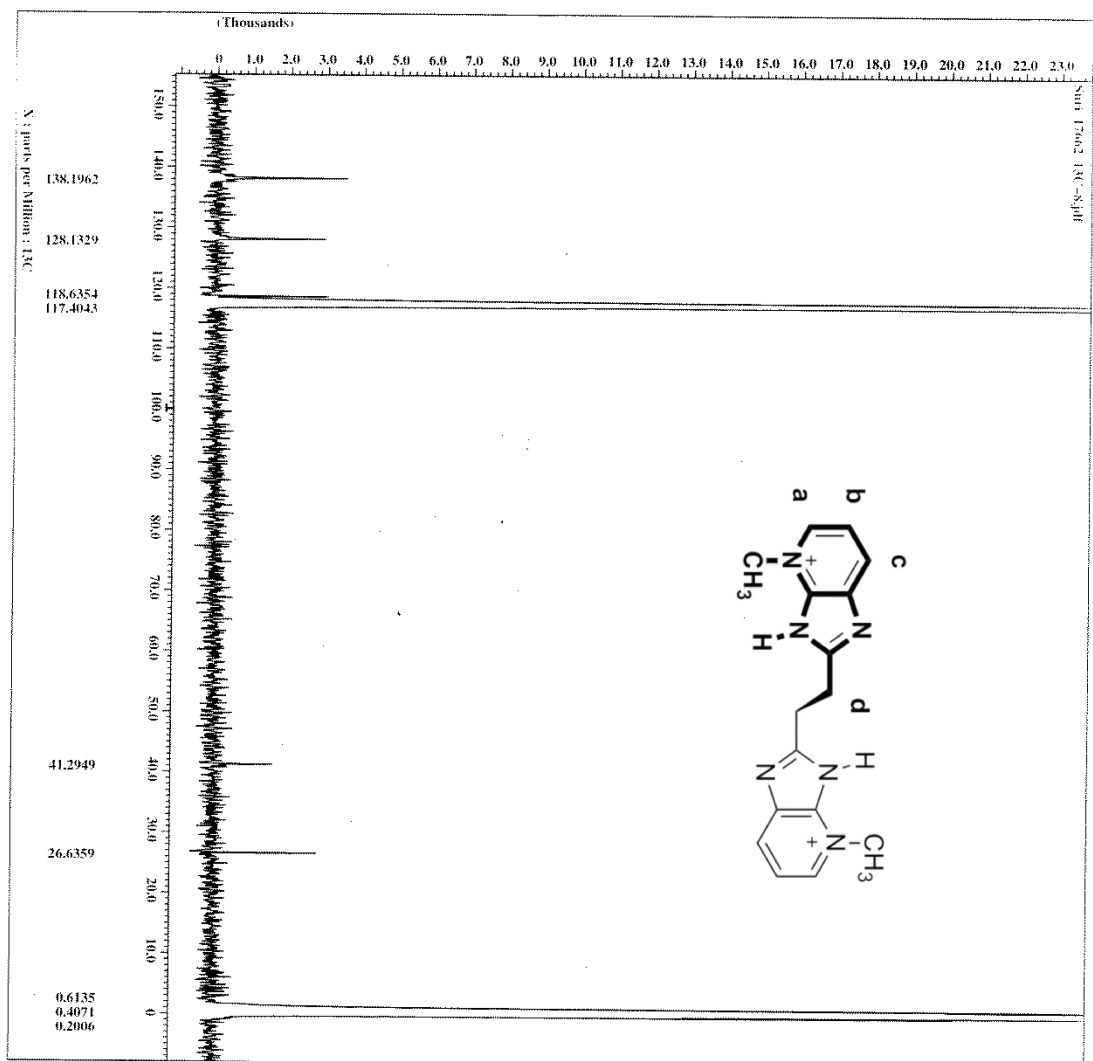
Compound $[3 \cdot \text{Me}_2][\text{CF}_3\text{SO}_3]_2$ ^1H NMR (CD_3CN , 400 MHz)



Compound $[3 \cdot \text{Me}_2][\text{CF}_3\text{SO}_3]_2$ COSY ^1H - ^1H (CD_3CN , 400 MHz)

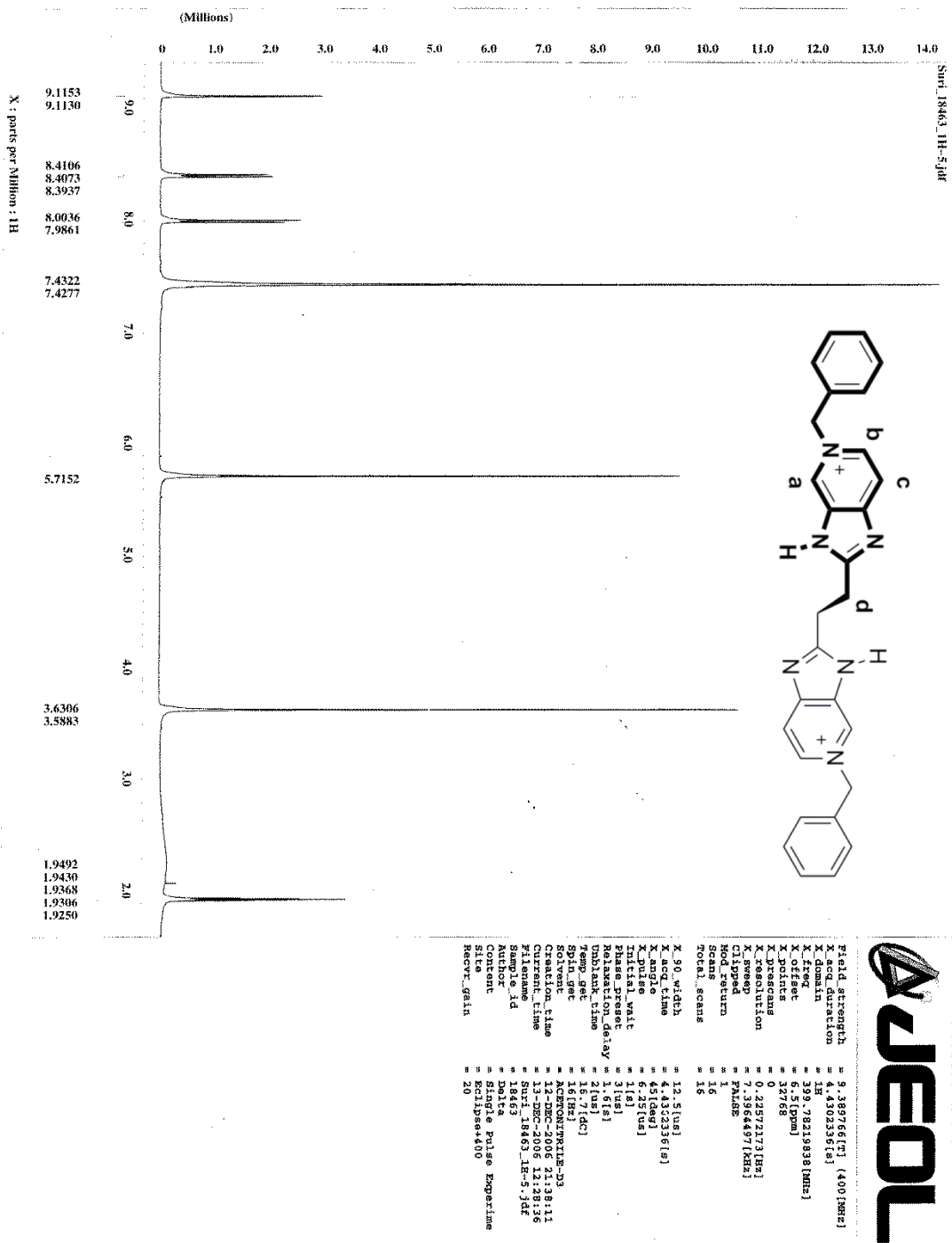


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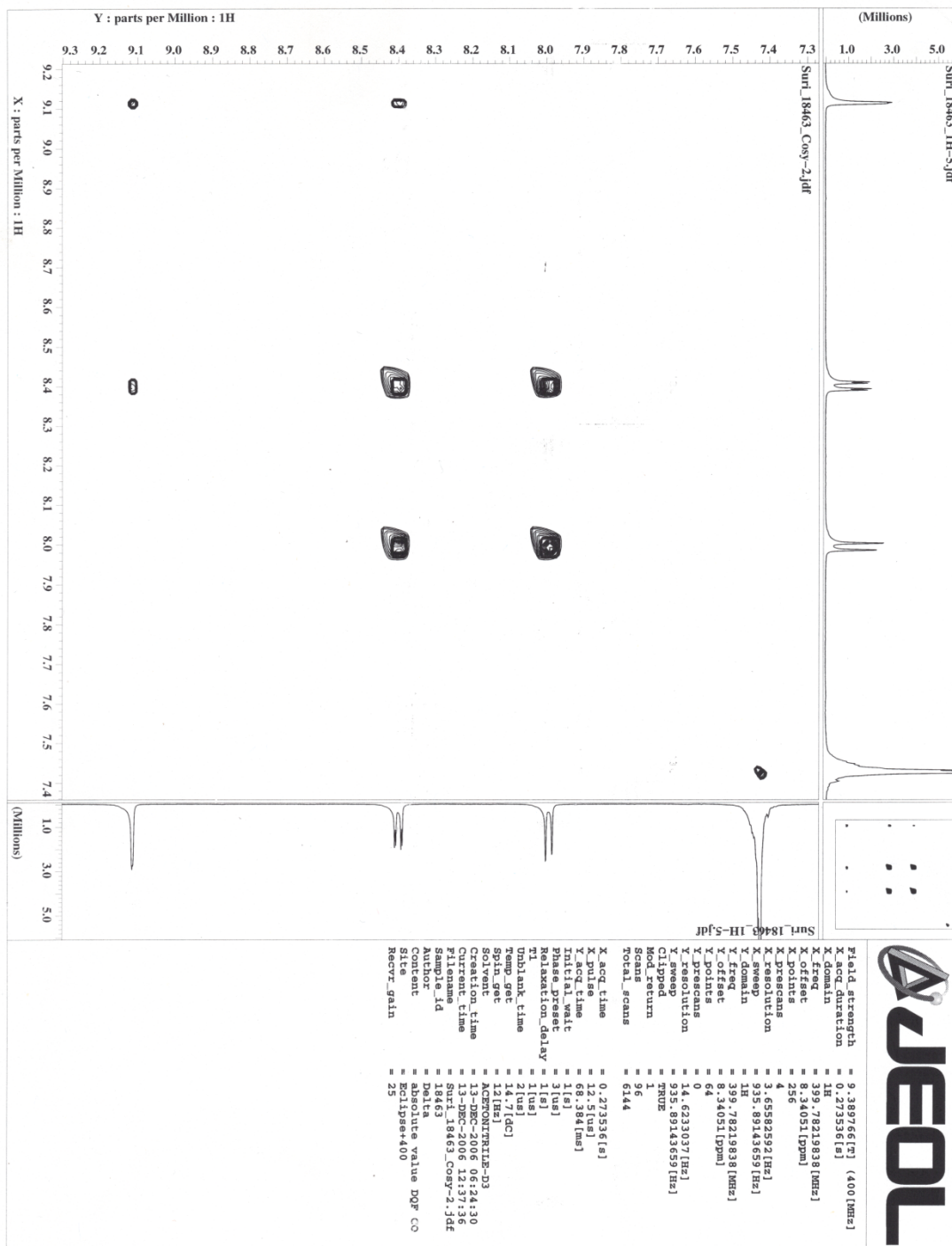


JEOL

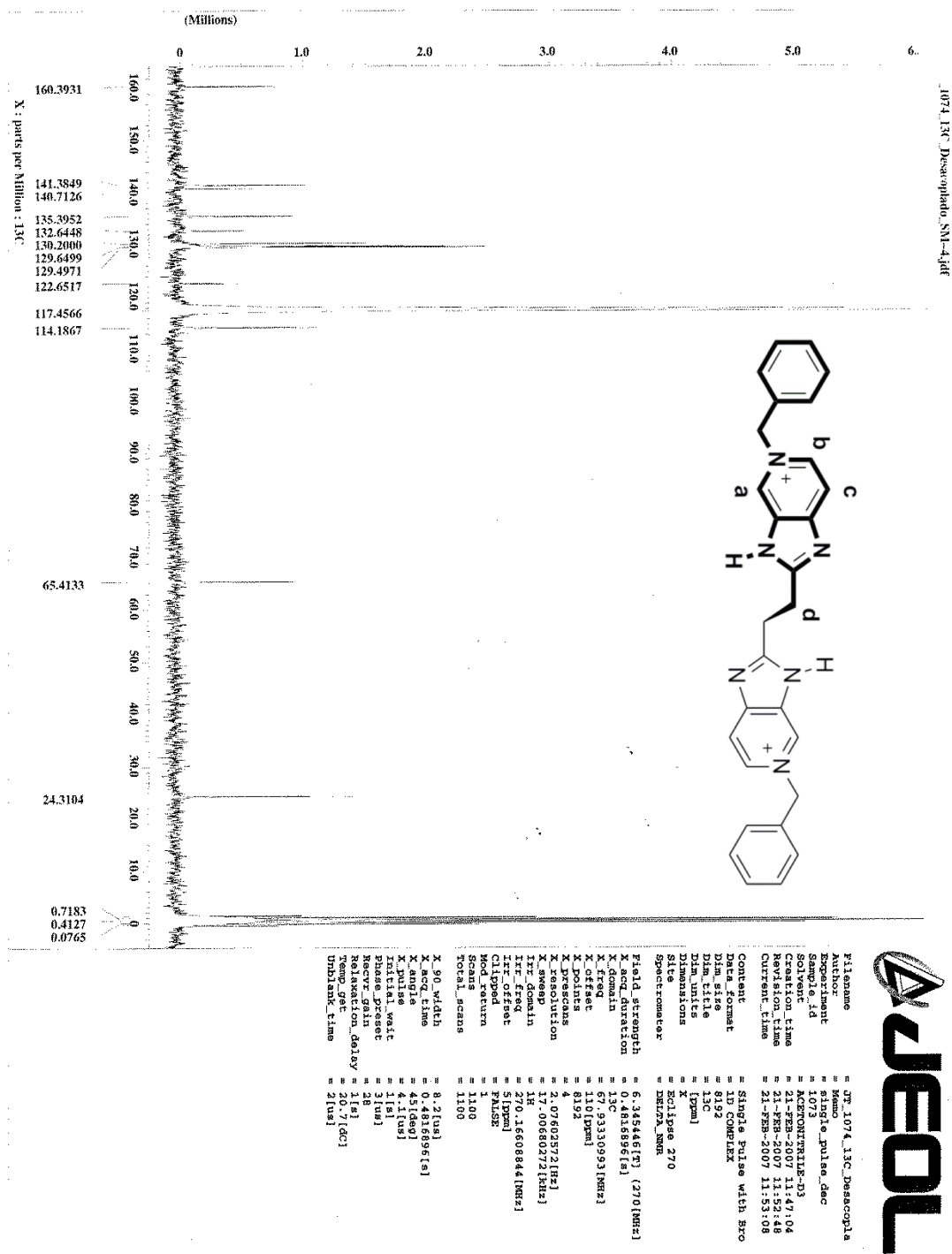
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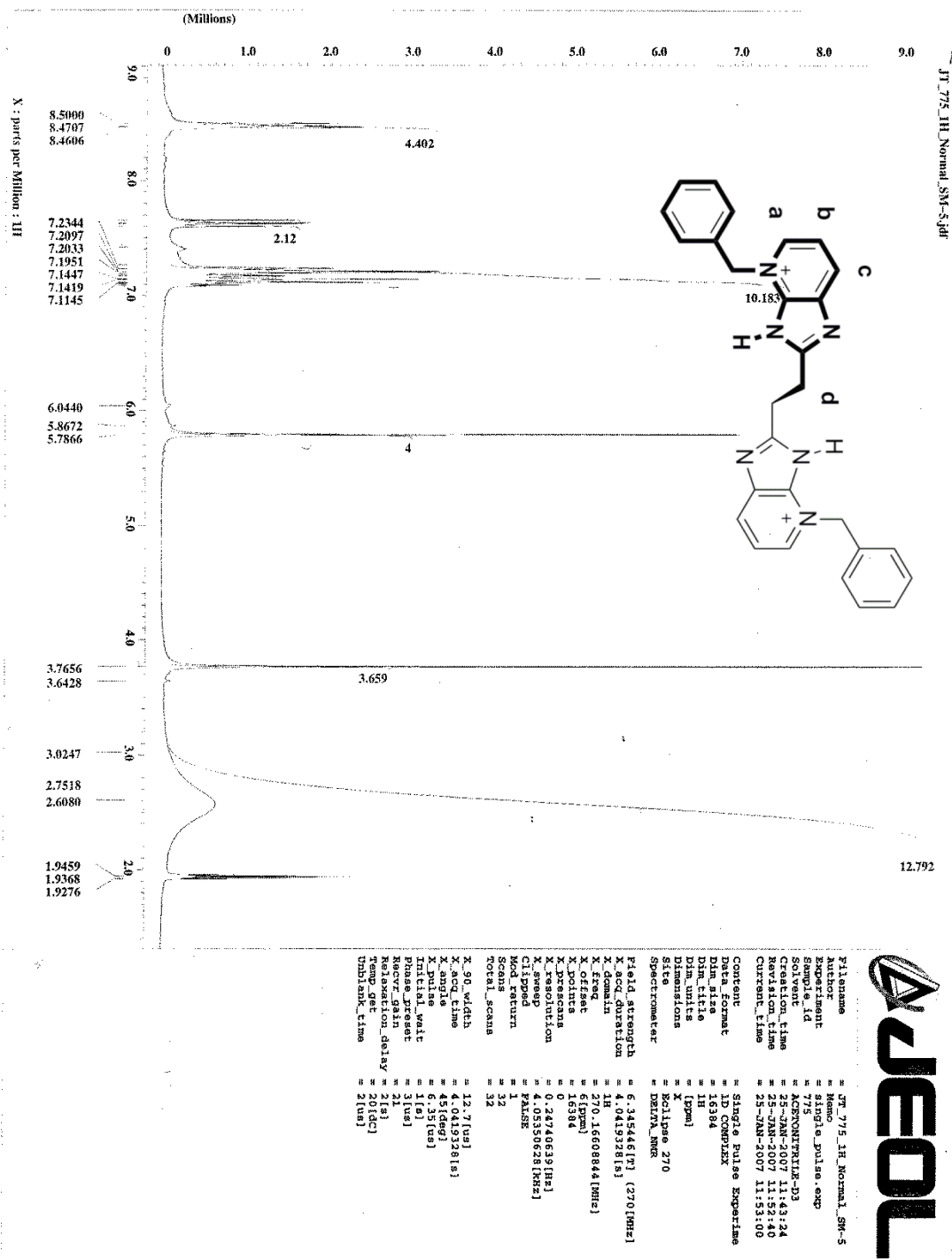
Compound $[2 \cdot \text{Bn}_2][\text{CF}_3\text{SO}_3]_2$ COSY ^1H - ^1H NMR (CD_3CN , 400 MHz)



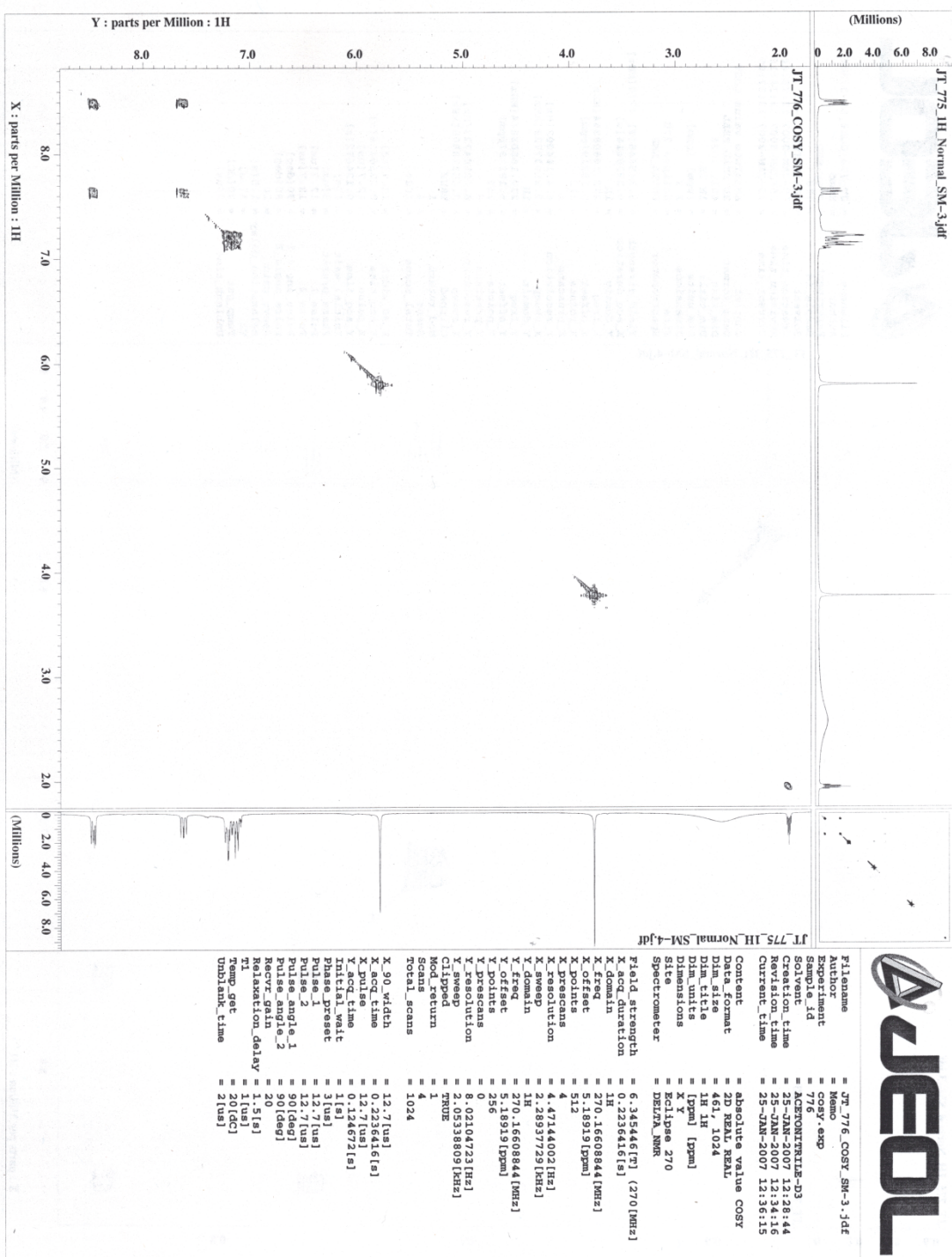
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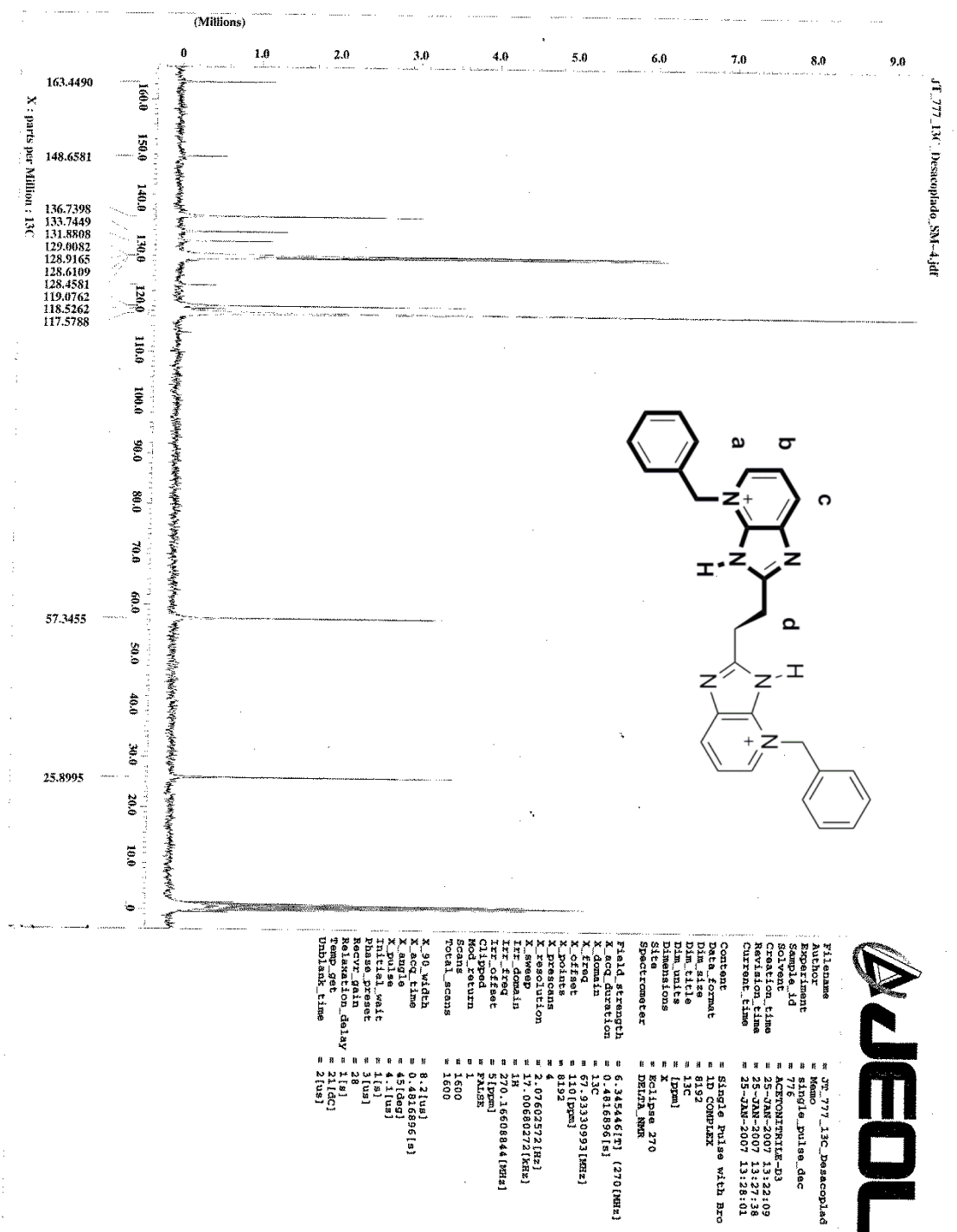
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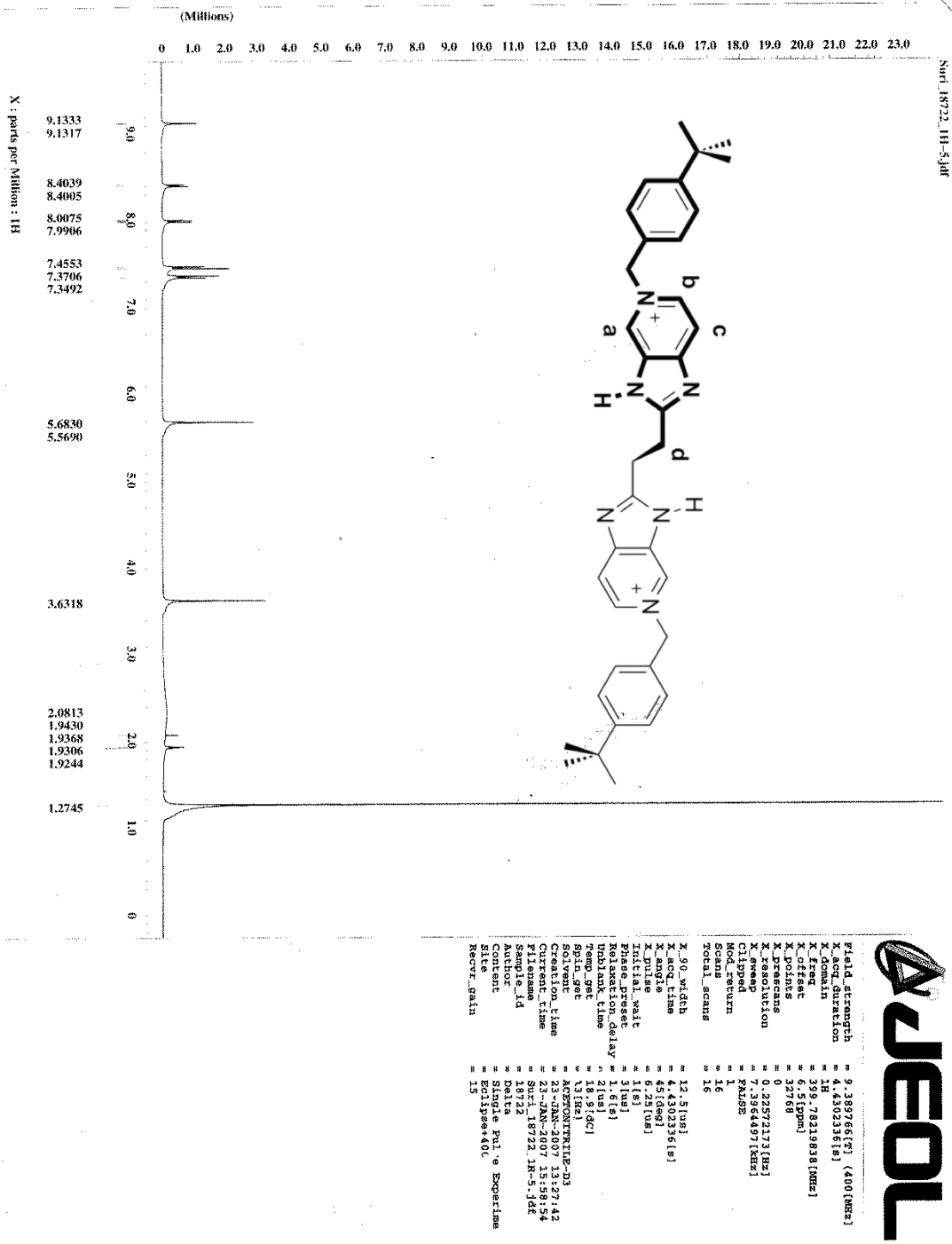
Compound $[3 \cdot \text{Bn}_2][\text{CF}_3\text{SO}_3]_2$ COSY ^1H - ^1H (CD_3CN , 270 MHz)



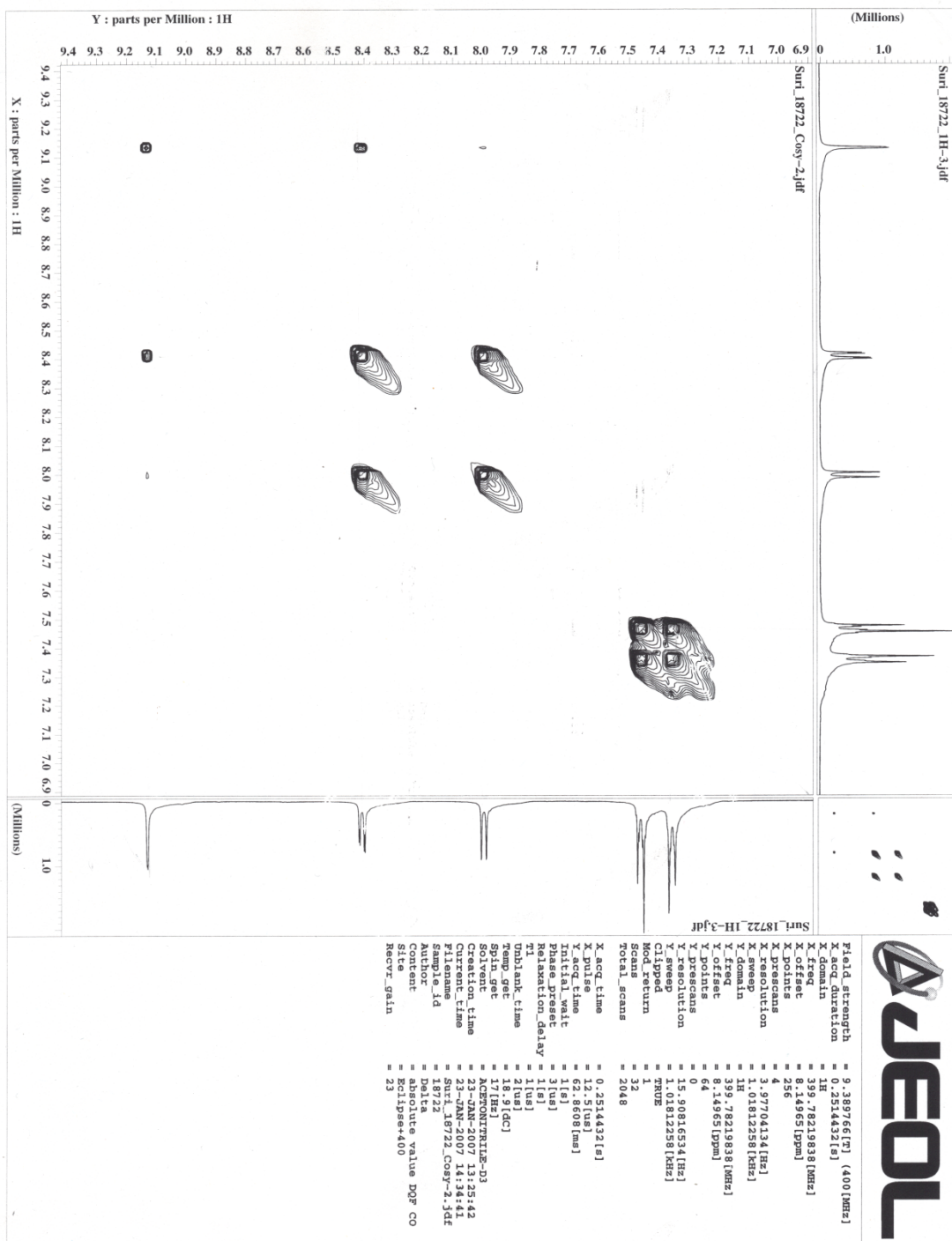
Compound $[3 \cdot \text{Bn}_2][[\text{CF}_3\text{SO}_3]_2$ ^{13}C NMR (CD_3CN , 68 MHz)



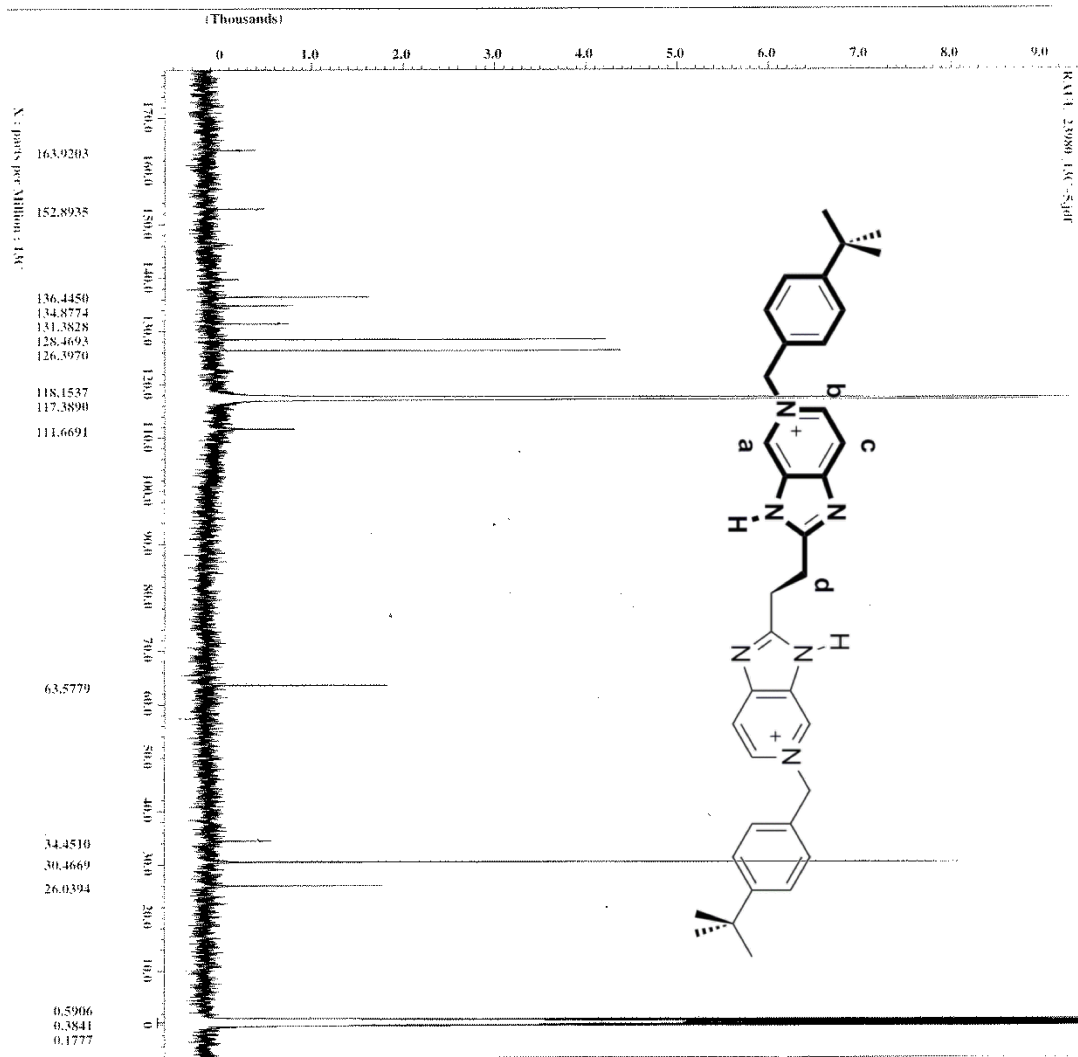
Compound **[2·(*t*BuBn)₂][CF₃SO₃]₂** ¹H NMR (CD₃CN 400 MHz)



Compound **[2·(*t*BuBn)₂][CF₃SO₃]₂** COSY ¹H-¹H (CD₃CN, 400 MHz)



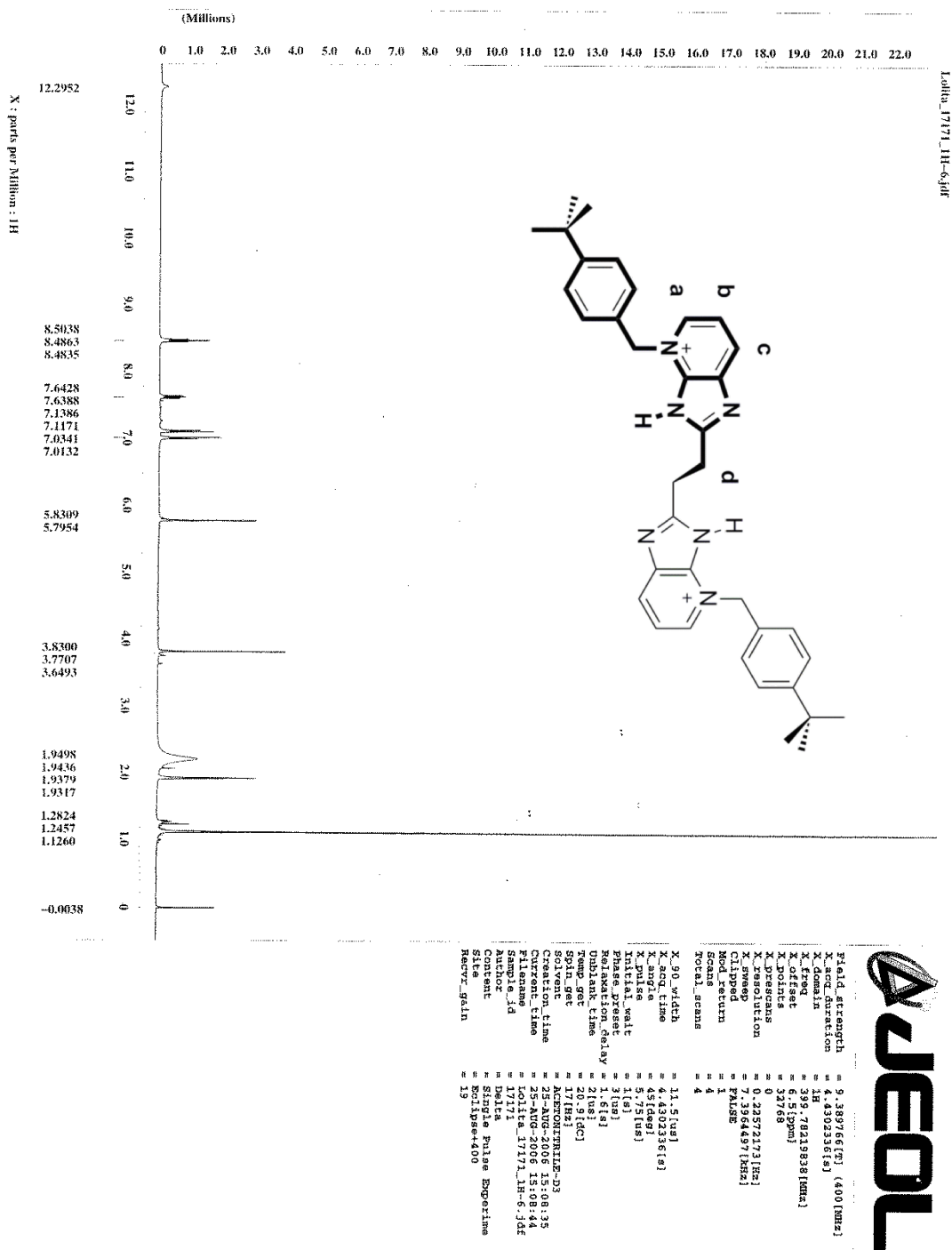
Compound $[2 \cdot (t\text{BuBn})_2][\text{CF}_3\text{SO}_3]_2$ ^{13}C NMR (CD_3CN 100 MHz)



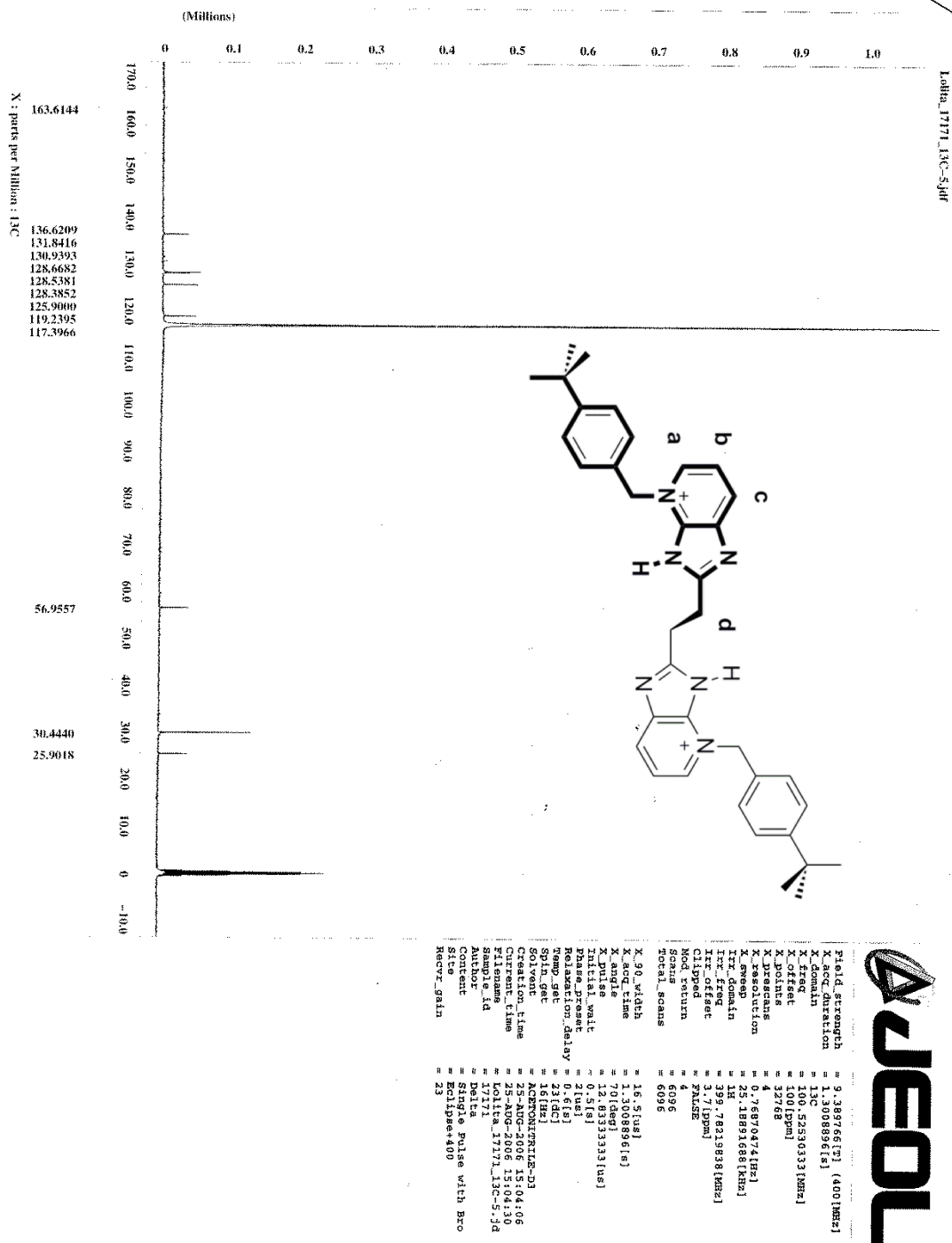
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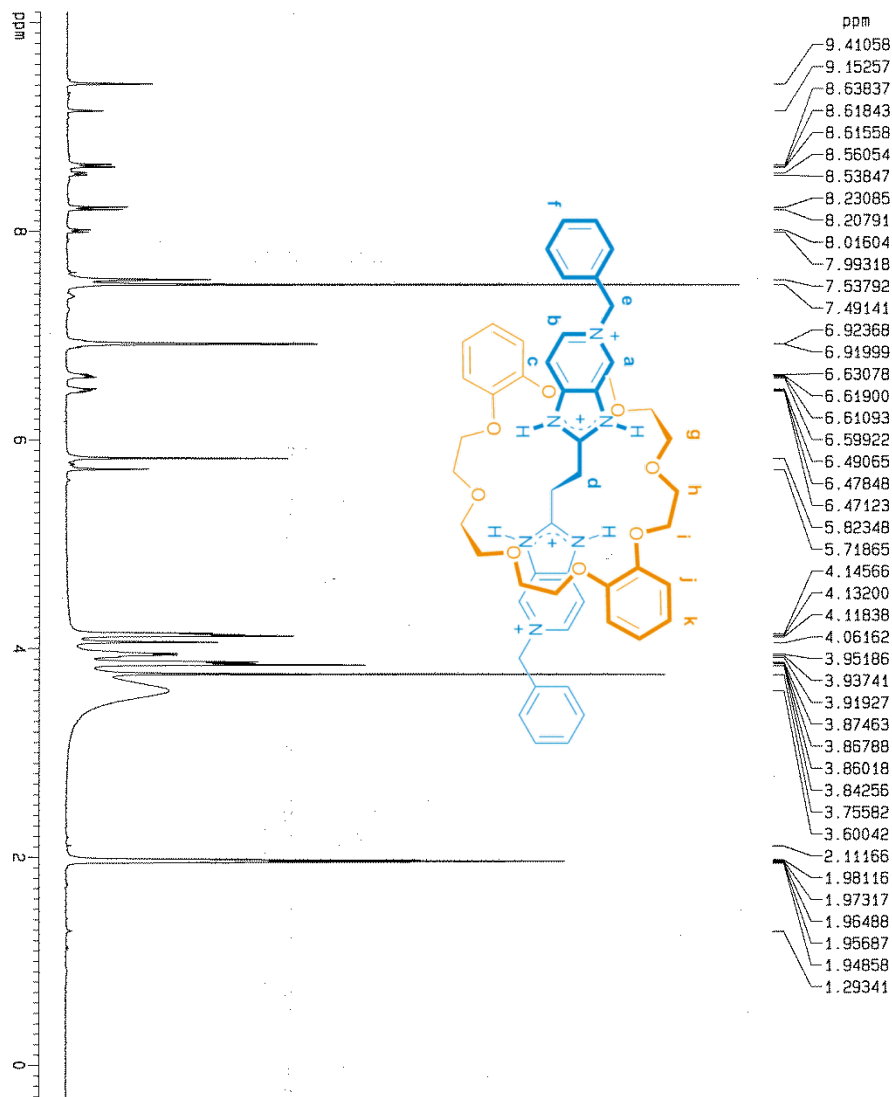
Compound **[3·(*t*BuBn)₂][CF₃SO₃]₂** ¹H NMR (CD₃CN 400 MHz)



Compound $[3 \cdot (t\text{BuBn})_2][\text{CF}_3\text{SO}_3]_2$ ^{13}C NMR (CD_3CN 100 MHz)



Compound $\{[2 \cdot \text{Bn}_2\text{H}_2]\text{CDB24C8}\}[\text{CF}_3\text{SO}_3]_4$ ^1H NMR (CD_3CN 300 MHz)



Brucker 300
 ^1H M-1
 Ivan S.

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 D1 1.0090000 sec

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Continuous Variation Method for complexation of $[2\cdot\text{H}_4][\text{CF}_3\text{SO}_3]_4$, $[3\cdot\text{H}_4][\text{CF}_3\text{SO}_3]_4$ and $[2\cdot\text{Me}_2\text{H}_2][\text{CF}_3\text{SO}_3]_4$ with DB24C8 by ^1H NMR in CD_3CN

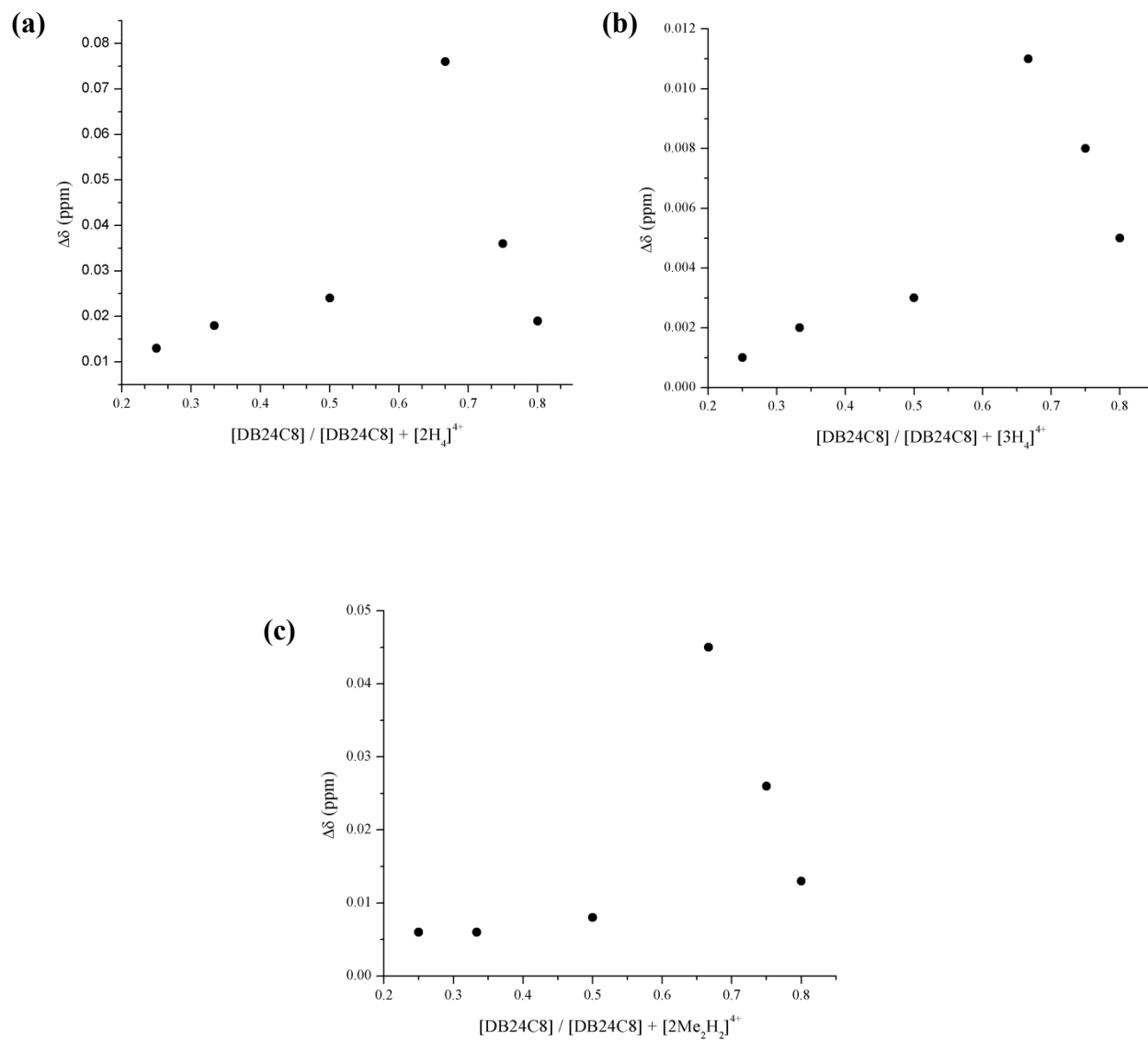


Figure S1. Job's plots for complexation of DB24C8 with (a) $[2\cdot\text{H}_4]^{4+}$, (b) $[3\cdot\text{H}_4]^{4+}$ and (c) $[2\cdot\text{Me}_2\text{H}_2]^{4+}$.

^1H NMR titration between $[2\cdot\text{H}_4]^{4+}$, $[3\cdot\text{H}_4]^{4+}$ and $[2\cdot\text{Me}_2\text{H}_2]^{4+}$ 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 $[2\cdot\text{H}_2][\text{CF}_4\text{SO}_3]_2$ in CD_3CN . Twenty aliquots of 2.0×10^{-4} M of **DB24C8** in CD_3CN were consecutively added and individual ^1H NMR spectra were recorded on a 300 MHz spectrophotometer at 25 °C. Identical procedures were carried out for compounds $[3\cdot\text{H}_2][\text{CF}_4\text{SO}_3]_2$ and $[2\cdot\text{Me}_2\text{H}_2][\text{CF}_4\text{SO}_3]_2$. Chemical shifts for protons H_b of the three axes were submitted to a least-square fitting analysis with the software WinEQNMR2¹ 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.

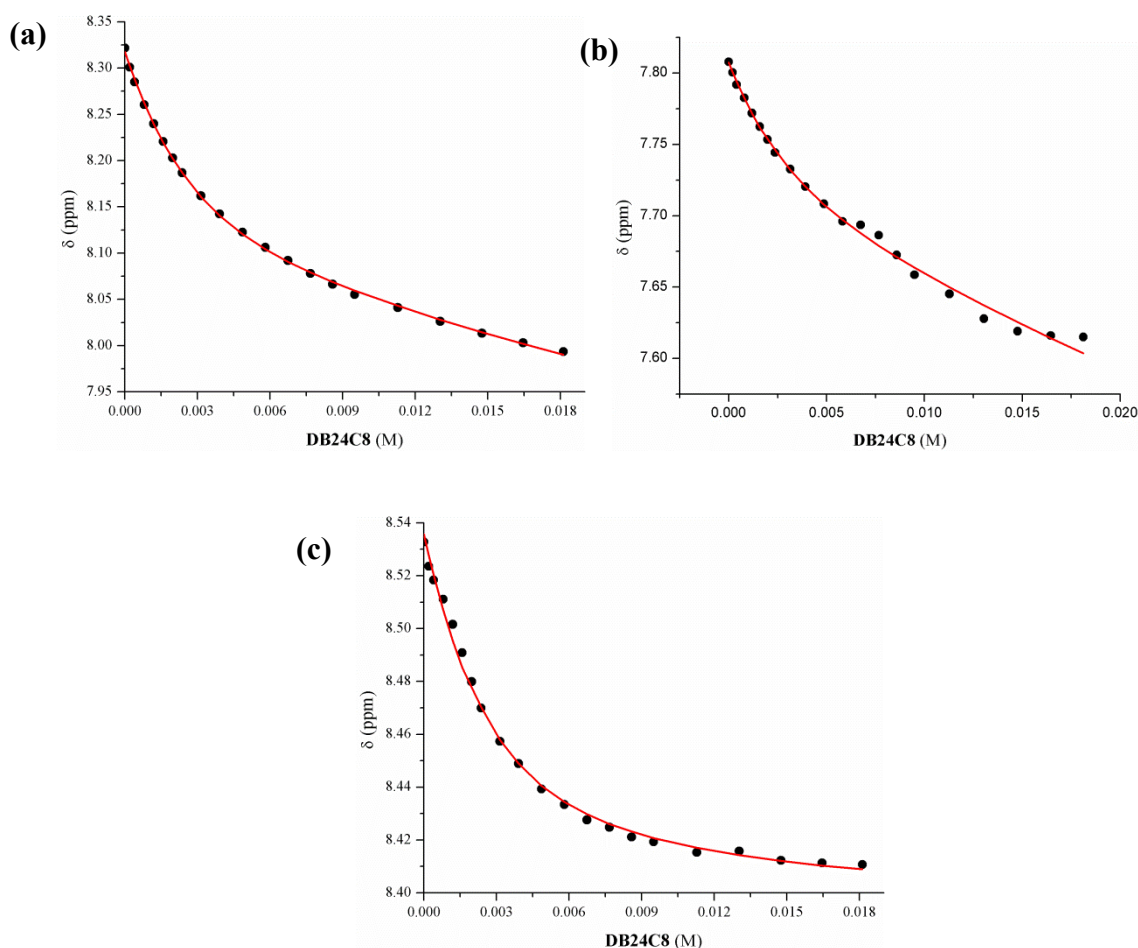


Figure S2. Chemical shifts of aromatic H_b proton of compounds (a) $[2\cdot\text{H}_2][\text{CF}_4\text{SO}_3]_2$, (b) $[3\cdot\text{H}_2][\text{CF}_4\text{SO}_3]_2$ and (c) $[2\cdot\text{Me}_2\text{H}_2][\text{CF}_4\text{SO}_3]_2$ in the titration with **DB24C8** in acetonitrile- d_3 .

NOESY of compound $\{[2 \cdot \text{Me}_2\text{H}_2] \cdot \text{CDB24C8}\} [\text{CF}_3\text{SO}_3]_4$

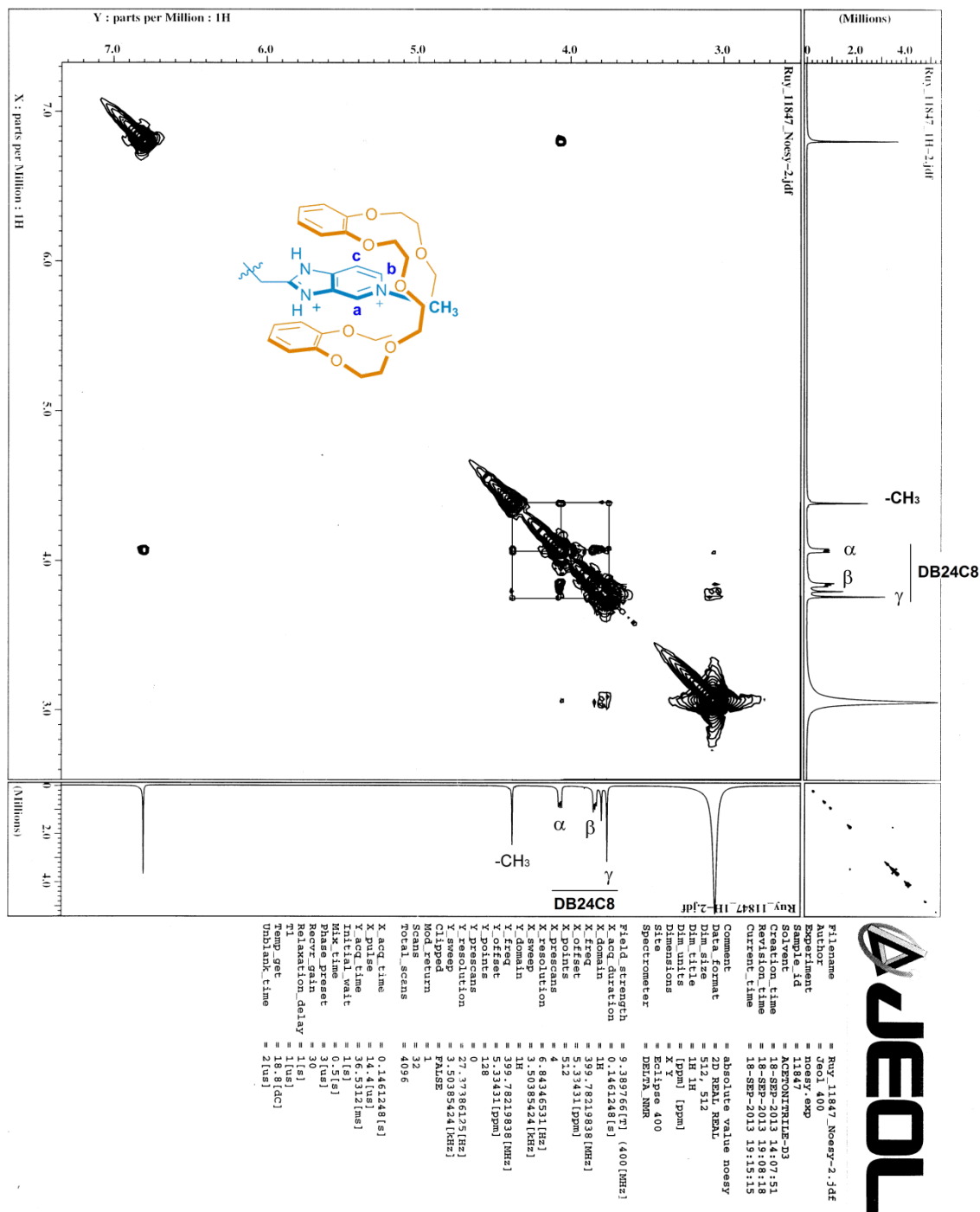


Figure S3. NOESY of $\{[2 \cdot \text{Me}_2\text{H}_2] \cdot \text{DB24C8}\} [\text{CF}_3\text{SO}_3]_4$ (CD_3CN , 400 MHz).

Details of Crystal Structure Determination for compounds $[2 \cdot \text{Bn}_2][\text{CF}_3\text{SO}_3]_2 \cdot \text{H}_2\text{O}$, $[3 \cdot \text{Bn}_2]\text{Br}_2 \cdot \text{CHCl}_3$ and $\{[2 \cdot \text{Bn}_2\text{H}_2]\text{CDB24C8}\}[\text{CF}_3\text{SO}_3]_4$

Crystals were grown by slow evaporation of: i) saturated aqueous solution of axle $[2 \cdot \text{Bn}_2][\text{CF}_3\text{SO}_3]_2$, ii) axle $[3 \cdot \text{Bn}_2]\text{Br}_2$ in an $\text{CH}_3\text{CN}/\text{CHCl}_3$ solvent mixture and iii) saturated solution containing $[2 \cdot \text{Bn}_2\text{H}_2][\text{CF}_3\text{SO}_3]_4$ 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 $[2 \cdot \text{Bn}_2][\text{CF}_3\text{SO}_3]_2 \cdot \text{H}_2\text{O}$, $[3 \cdot \text{Bn}_2]\text{Br}_2 \cdot \text{CHCl}_3$ and $\{[2 \cdot \text{Bn}_2\text{H}_2]\text{CDB24C8}\}[\text{CF}_3\text{SO}_3]_4$.

	$[2 \cdot \text{Bn}_2][\text{CF}_3\text{SO}_3]_2 \cdot \text{H}_2\text{O}$	$[3 \cdot \text{Bn}_2]\text{Br}_2 \cdot \text{CHCl}_3$	$\{[2 \cdot \text{Bn}_2\text{H}_2]\text{CDB24C8}\}[\text{CF}_3\text{SO}_3]_4$
Formula	$\text{C}_{30}\text{H}_{30}\text{F}_6\text{N}_6\text{O}_8\text{S}_2$	$\text{C}_{29}\text{H}_{27}\text{Cl}_3\text{Br}_2\text{N}_6$	$\text{C}_{56}\text{H}_{60}\text{F}_{12}\text{N}_6\text{O}_{20}\text{S}_4$
formula weight	780.72	725.74	1493.34
crystal system	monoclinic	monoclinic	monoclinic
space group	$P21/c$	$P21/n$	$P21/n$
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/restraints	243/0	361/0	442/0
Min/max residual	0.32/-0.28	0.77 /-0.79	0.59/-0.34
density [e/Å ³]			

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|;$$

$$^b R_2w = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}, \text{ where } w = q[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}.$$

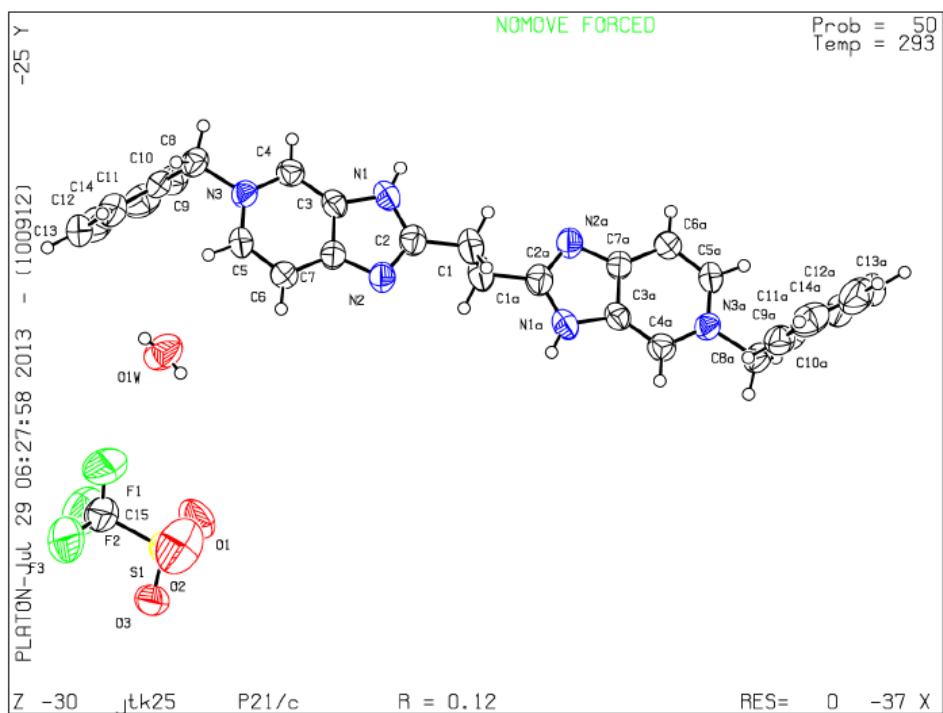


Figure S4. ORTEP representation of compound $[2 \cdot \text{Bn}_2][\text{CF}_3\text{SO}_3]_2 \cdot \text{H}_2\text{O}$.

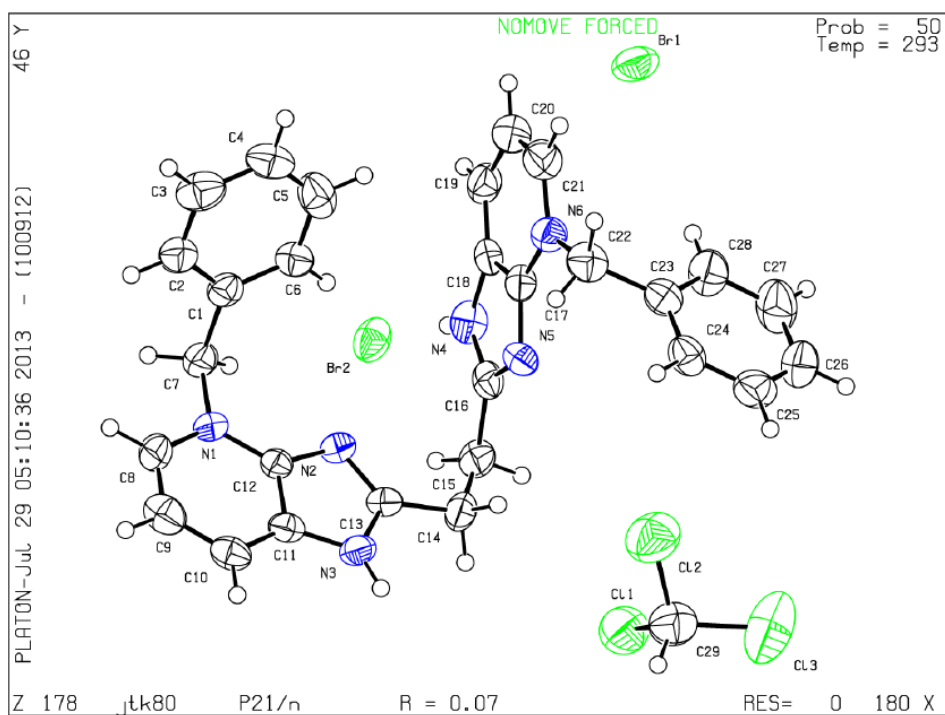


Figure S5. ORTEP representation of compound $[3 \cdot \text{Bn}_2]\text{Br}_2 \cdot \text{CHCl}_3$.

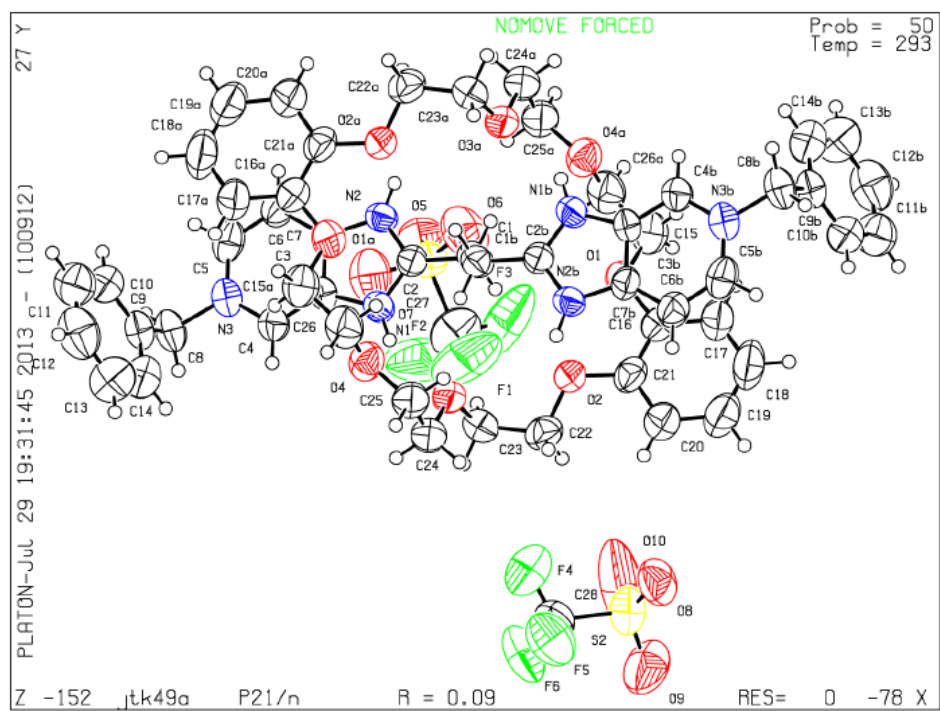


Figure S6. ORTEP representation of compound $\{[2 \cdot \text{Bn}_2\text{H}_2]\text{CDB24C8}\}[\text{CF}_3\text{SO}_3]_4$.