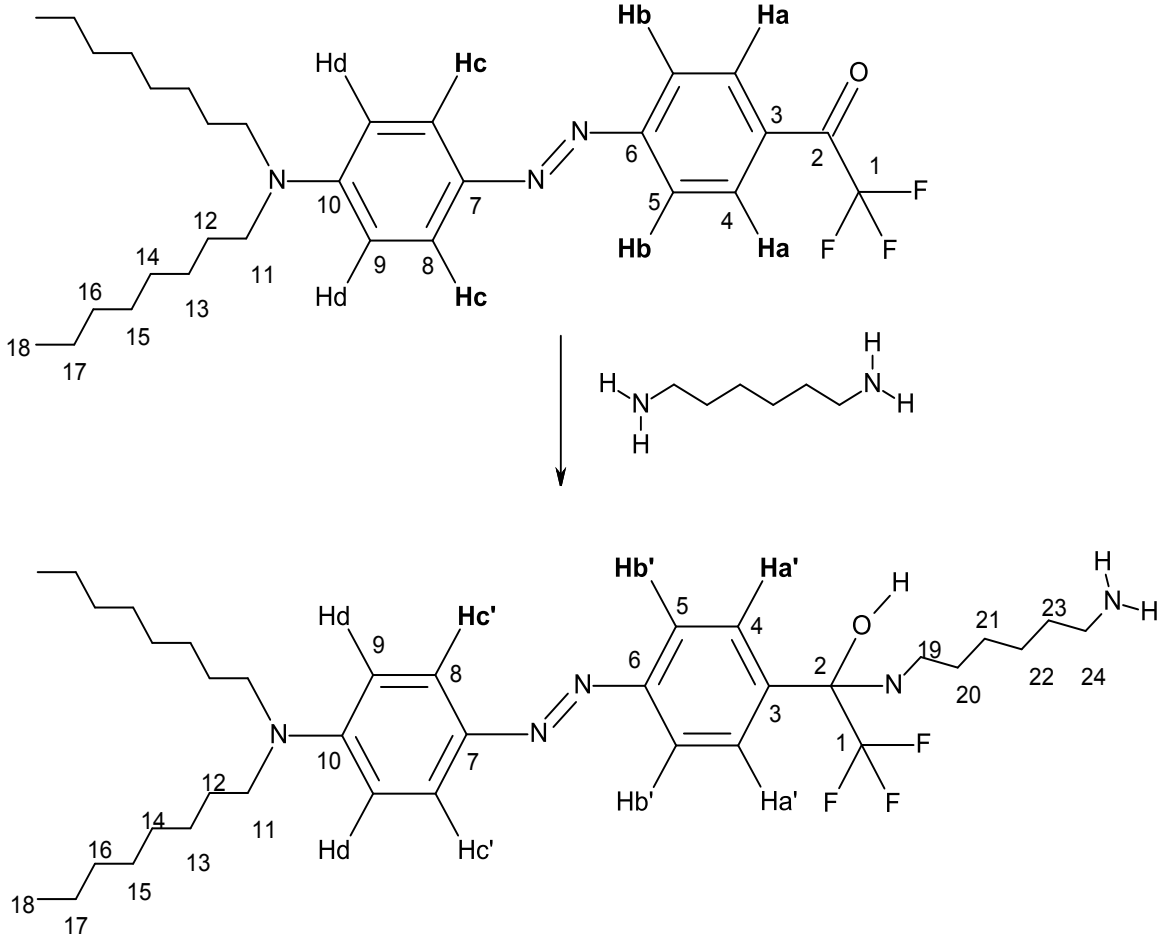
Supplementary information to "Trifluoroacetylazobenzene for optical and electrochemical detection of amines" by Jhih-Fong Lin et al.

1H-NMR and 13C-NMR spectroscopy analyses

The dye amine adduct were characterized using nuclear magnetic resonance spectroscopy (NMR) Bruker AV 400. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-400 and calibrated using the residual peak of solvents as an internal standard [$CDCl_3$ ($CHCl_3$ δH 7.26 ppm, $CDCl_3$ δC 77.0 ppm). The dye was dissolved in $CDCl_3$ and different concentration of amine was added. Spectrum was taken 20 min after addition.



Scheme S1

The reaction of dye with different amines (cadaverine, putrescine, ethylamine and ammonia) was also Ha (δ ppm 8.16), Hb and Hc (δ ppm 7.87-7.92) protons of dye undergoes upfield shift upon reaction with the amine (for ^{1}H-NMR and ^{13}C-NMR spectra see data 1.1-1.25). New Ha', Hb' and Hc' in the dye amine adduct appeared in the range δ ppm 7.78-7.40.[1]

Imine or carbinolamine or aminal are the three possible products in the reaction of dye with amine. The study of ^{13}C-NMR of the dye and dye adduct indicates the carbinolamine formation. The quartet of carbonyl carbon at 180 ppm in the dye disappeared in the dye adduct and replaced by new quartet at 86 ppm for

carbinolamine in the adduct spectrum. This corroborates with the results reported by Mertz *et al.* (Table 2).[1] The imine carbon is expected to give quartet around 150 ppm.[2]
We determined the percentage of product (dye and amine adducts, amines: cadaverine, putrescine and ethylamine) and dye in the reaction mixture from integration values of hydrogens of the dye and product (**Table 1**).

Note, that product formation during the reaction of dye with ammonia even at high concentration of ammonia could not be detected.

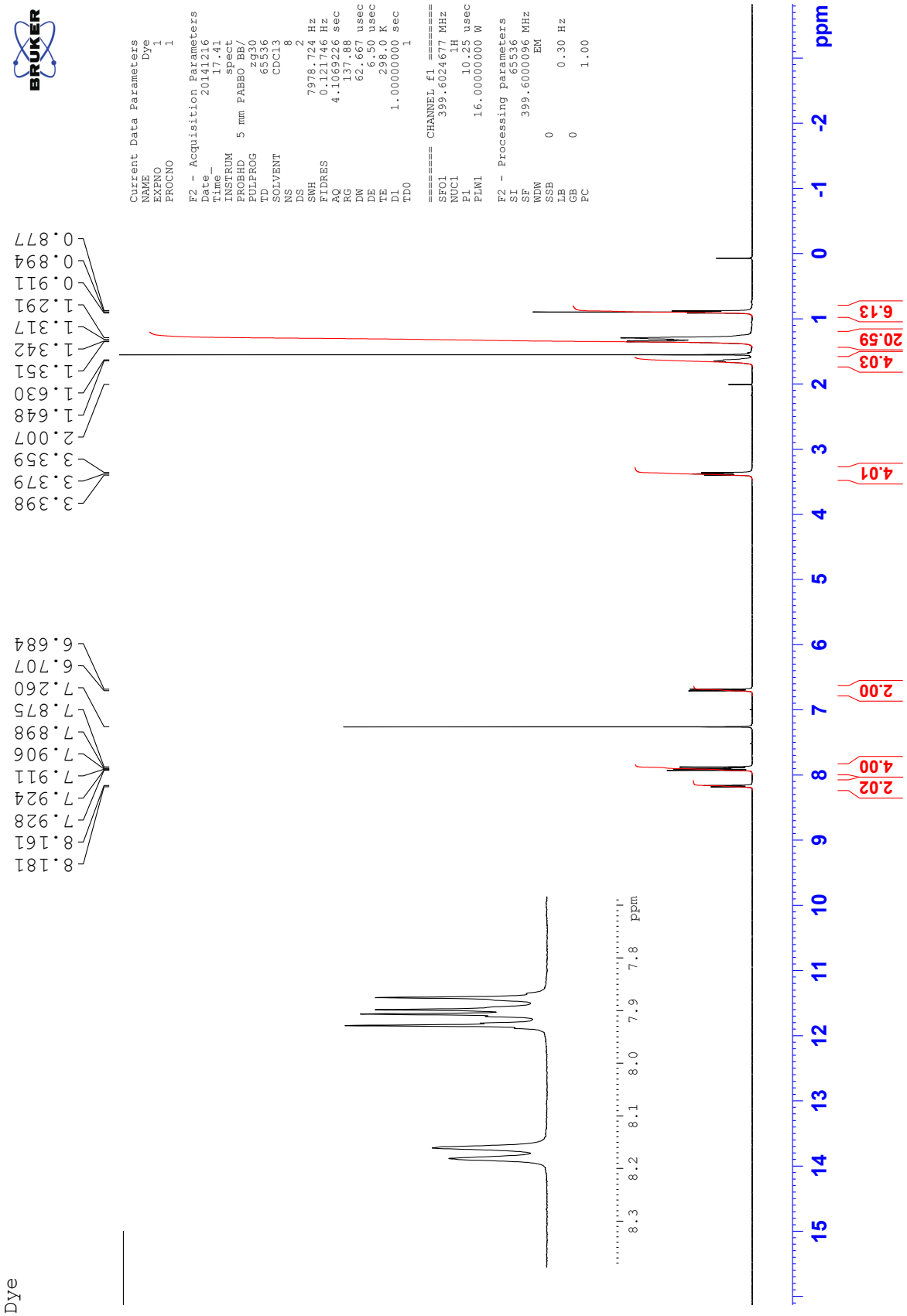
Table S1 Peak and integration values

Peak	**8.16 (d, J= 8Hz)** Expected integration : 2 hydrogens (**Ha protons**)	**7.87-7.92** Expected integration : 4 hydrogens (**Hb and Hc protons**)	**7.78-7.40** Expected integration : 6 hydrogens (**Ha', Hb', Hc' protons**)
Compound			
Dye	2	4	0
Dye + cadaverine (1:0.5 molar eqv.)	1.79(89.64%)	3.56(89.02%)	0.75 (12.48%)
Dye + cadaverine (1:1 molar eqv.)	1.50 (74.92%)	3.02 (75.41%)	1.42 (23.63%)
Dye + cadaverine (1:1.5 molar eqv.)	1.26 (63.00%	2.53 (63.25%)	2.19 (36.50%)
Dye + cadaverine (1:2 molar eqv.)	1.04 (52.00%)	2.13 (53.25%)	2.75 (45.83%)
Dye + cadaverine (1:3 molar eqv.)	0.91 (45.50%)	1.89 (47.25%)	3.15 (52.50%)
Dye + cadaverine (1:4 molar eqv.)	0.72 (36.00%)	1.49 (37.25%)	3.75 (62.50%)
Dye + cadaverine (1:8 molar eqv.)	0	0	6 (100 %)
Dye + putrescine (1:0.5 molar eqv.)	1.76 (88.00%)	Two peaks are not separated	
Dye + putrescine (1:1 molar eqv.)	1.56 (78.00%)		
Dye + putrescine (1:2 molar eqv.)	0.47 (23.5 %)		
Dye + putrescine (1:2.5 molar eqv.)	0.35 (17.50%)		
Dye + putrescine (1:3 molar eqv.)	0.34 (17.00%)		
Dye + putrescine (1:8 molar eqv.)	0	0	6 (100%)
Dye + ethyl amine (1:0.5 molar eqv.)	1.96 (98.00%)	3.91 (97.75)	0.13 (21.70%)
Dye + ethyl amine (1:1 molar eqv.)	1.91 (95.50%)	3.79 (94.75%)	0.27 (4.50%)
Dye + ethyl amine (1:2 molar eqv.)	1.80 (90.00%)	3.57 (89.25)	0.64 (10.66)
Dye + ethyl amine (1:3 molar eqv.)	1.74 (87.00%)	3.47 (86.75)	0.76 (12.67)
Dye + ethyl amine (1:4 molar eqv.)	1.62 (81.00%)	3.26 (81.50%)	1.03 (17.16%)
Dye + ethyl amine (1:8 molar eqv.)	1.54 (77.00%)	3.08 (77.00%)	1.35 (22.50%)
Percentage of dye in reaction mixture= (integration of Ha peak/2)* 100 Percentage of dye in reaction mixture = (integration of Hb and Hc peak/4)* 100 Percentage of product in reaction mixture = (integration of Ha', Hb' and Hc' peak/6)* 100			

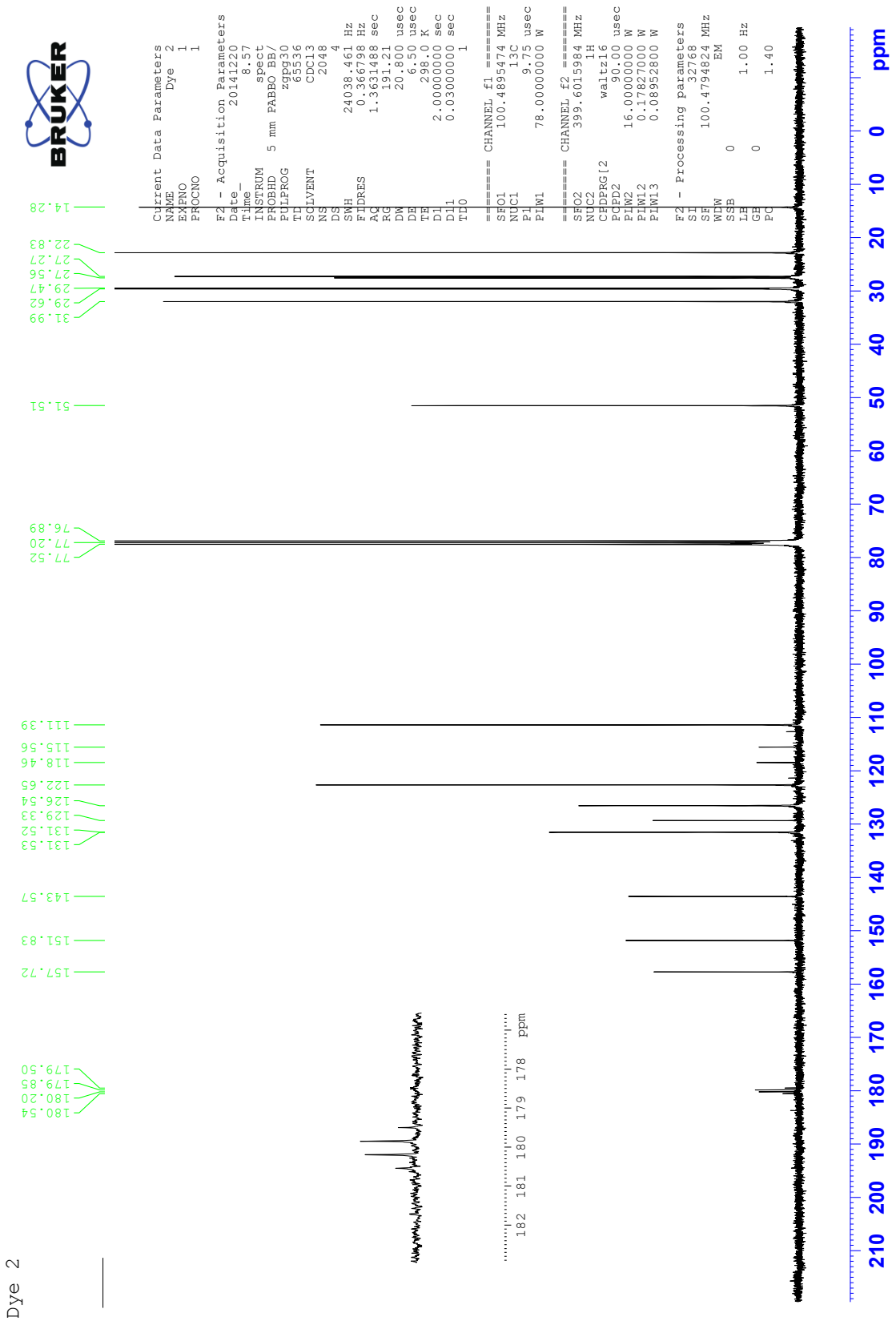
Table S2 ^{13}C chemical shifts of dye and dye adduct

Carbon	δppm of carbon	
	Dye	**Dye cadaverine adduct**
1	111.39, 115.56, 118.46, 122.65	121.25, 125.09, 128.79, 142.85
2	179.5, 179.85, 180.20, 180.54	85.90, 86.19, 86.47, 86.76
3	131.53	137.37
4	131.52	125.09
5	129.33	121.25
6	151.83	150.40
7	143.57	142.85
8	126.65	125.09
9	111.39	110.78
10	157.79	153.24
11	51.51	50.89
12	31.99	31.57
13	29.62	29.22
14	29.47	29.06
15	27.47	26.87
16	27.27	26.87
17	22.83	22.41
18	14.28	13.87
19	--	41.37
20	--	23.97
21	--	
22	--	
23	--	
24	--	33.46

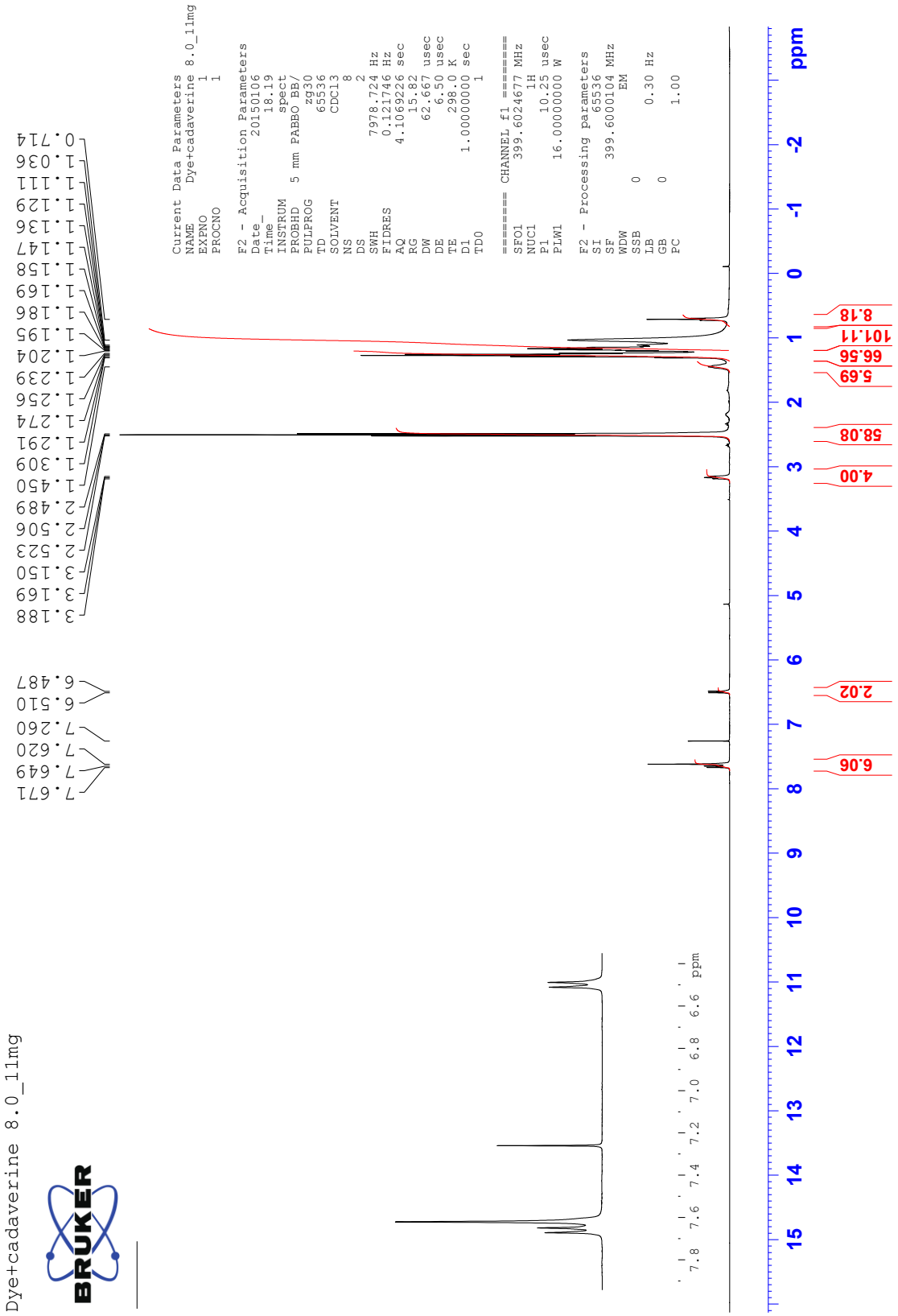
1.1 ^{1}H NMR Spectrum of Dye



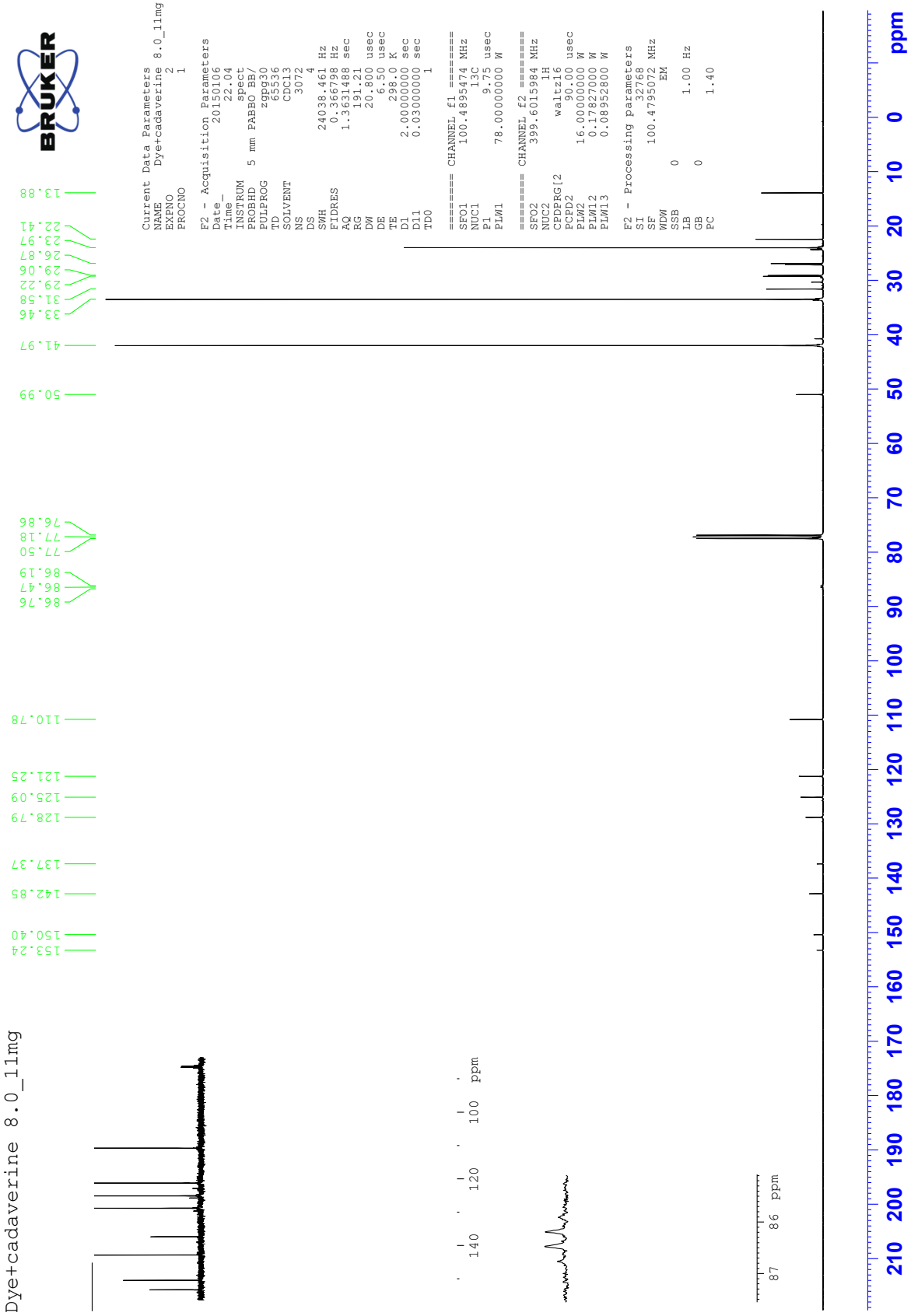
1.2 ^{13}C NMR Spectrum of Dye



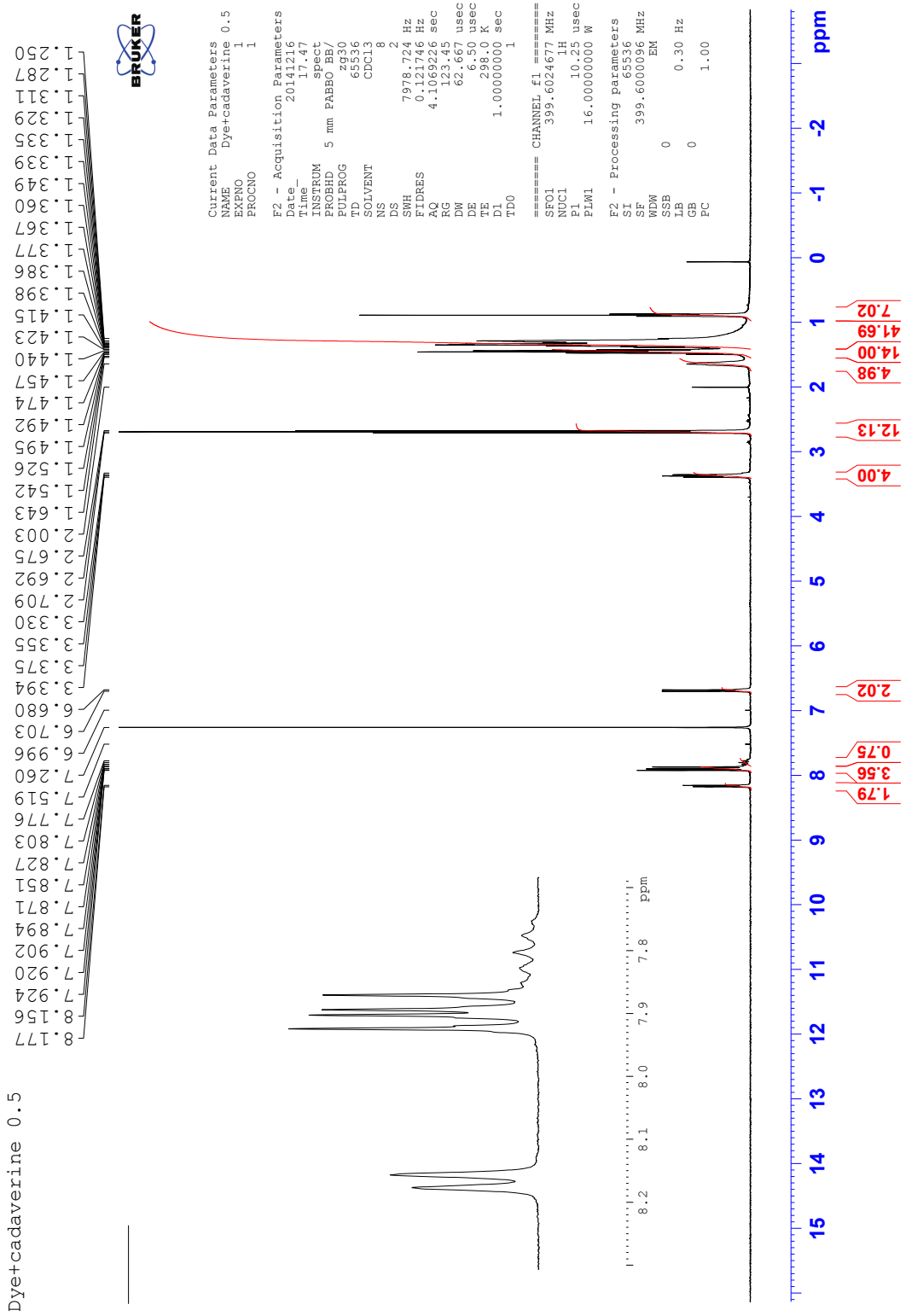
1.3 ^{1}H NMR Spectrum of Dye + cadaverine (1:8 eqv.) (spectrum taken after 20 min)



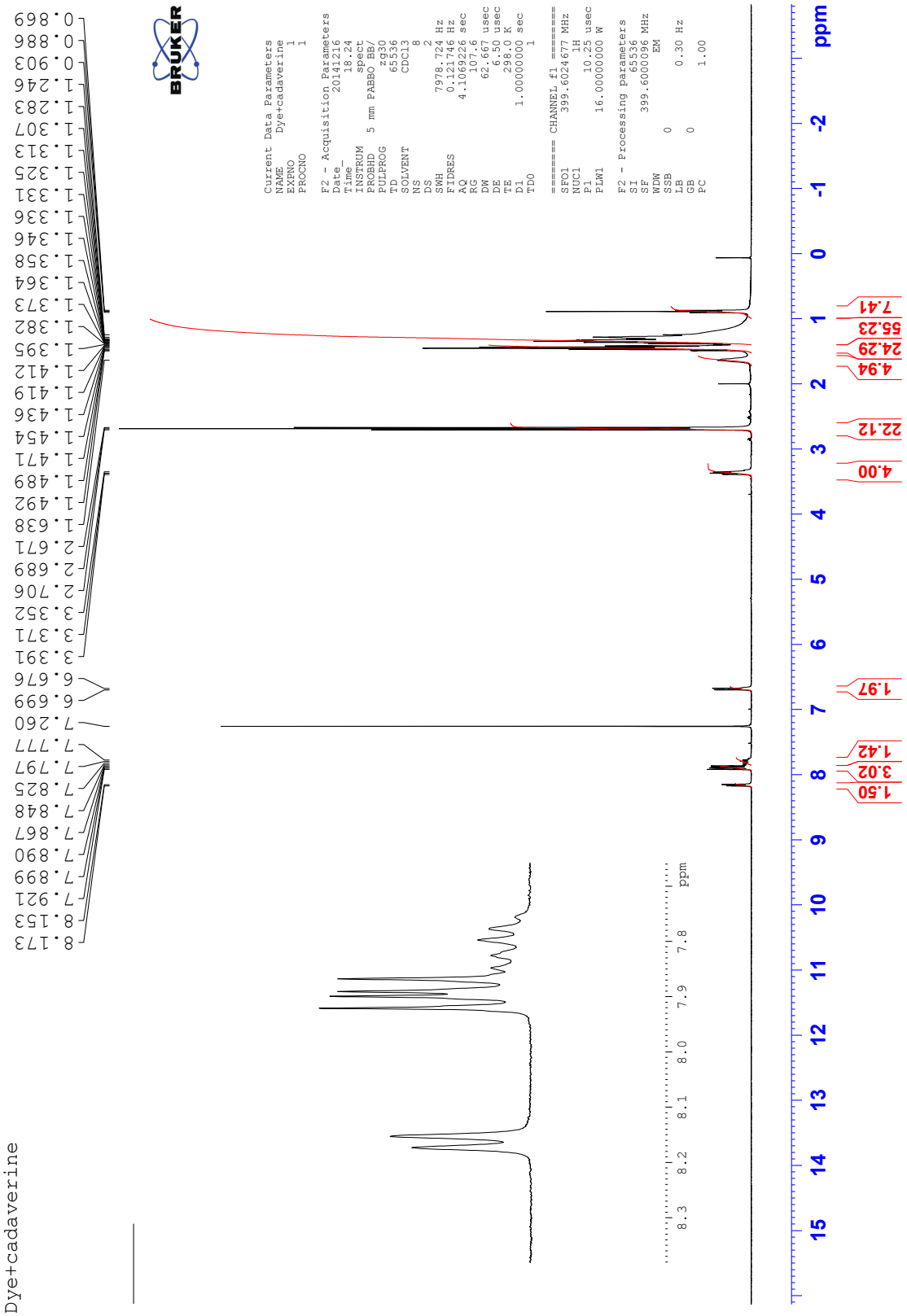
1.4 ^{13}C NMR Spectrum of Dye + cadaverine (1:8 eqv.) (spectrum taken after 4 h).



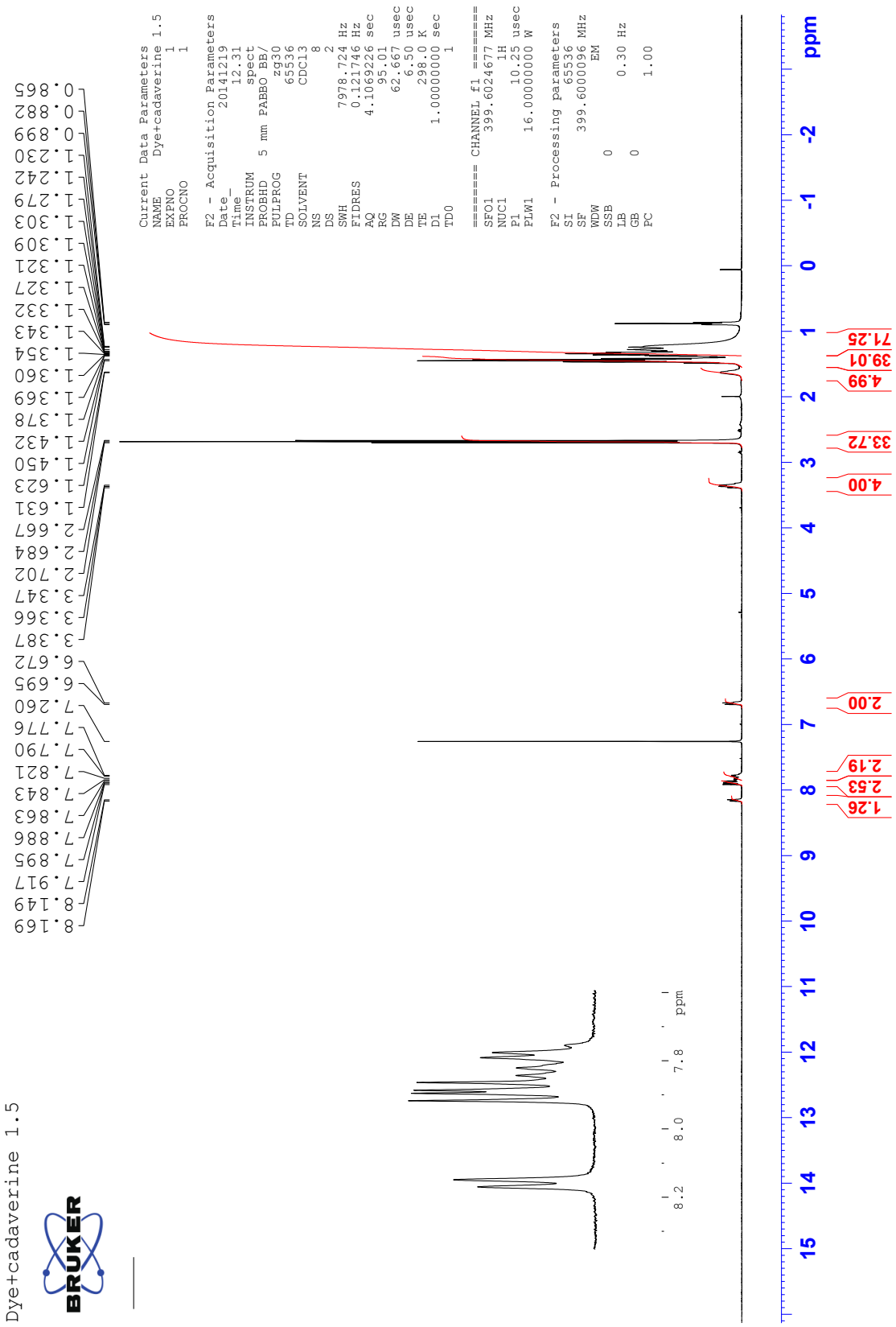
1.5 ^{1}H NMR Spectrum of Dye + cadaverine (1:0.5 eqv.) (spectrum taken after 20 min)



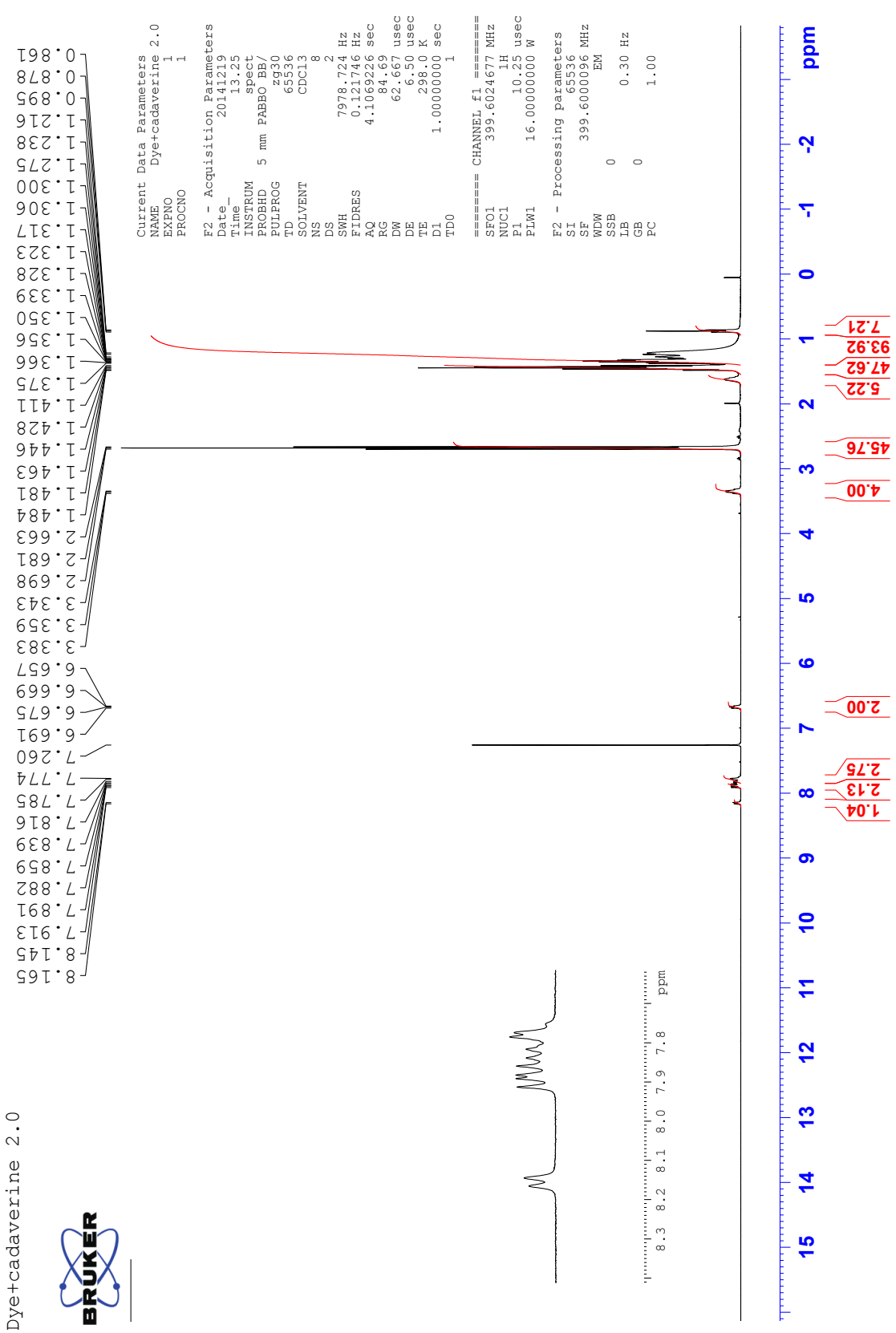
1.6 ^{1}H NMR Spectrum of Dye + cadaverine (1:1 eqv.) (spectrum taken after 20 min)



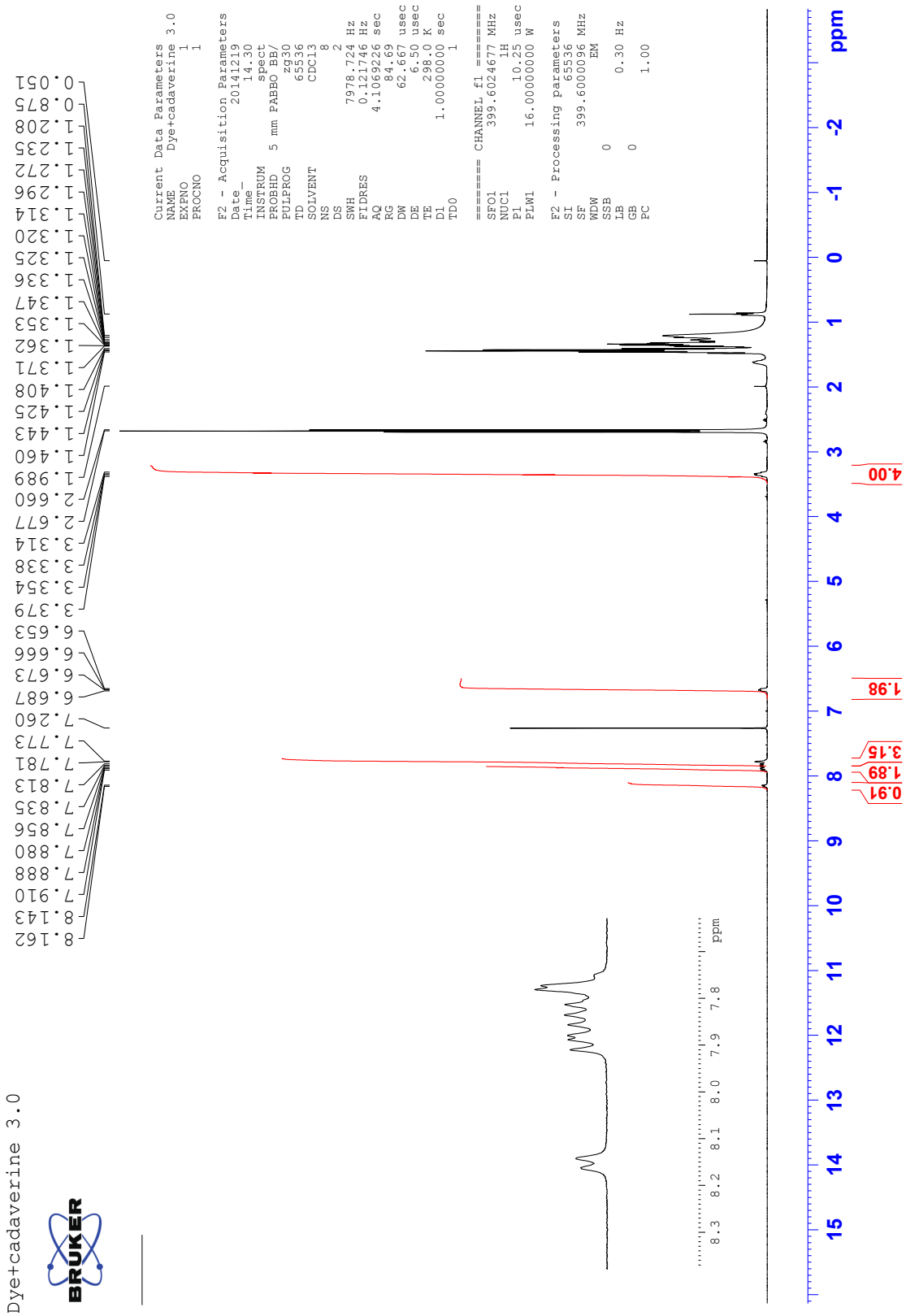
1.7 ^{1}H NMR Spectrum of Dye + cadaverine (1:1.5 eqv.) (spectrum taken after 20 min)



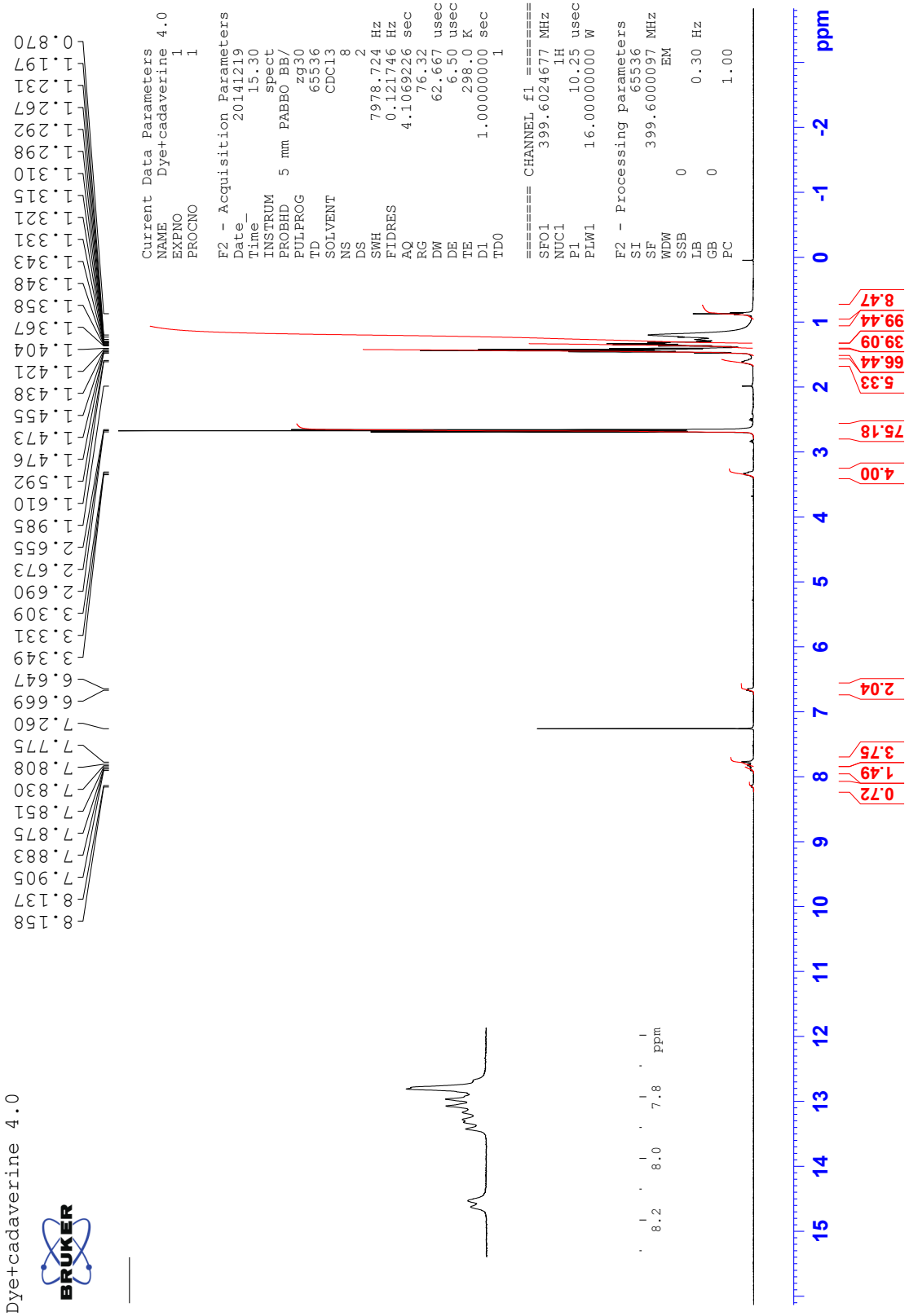
1.8 ^{1}H NMR Spectrum of Dye + cadaverine (1:2 eqv.) (spectrum taken after 20 min)



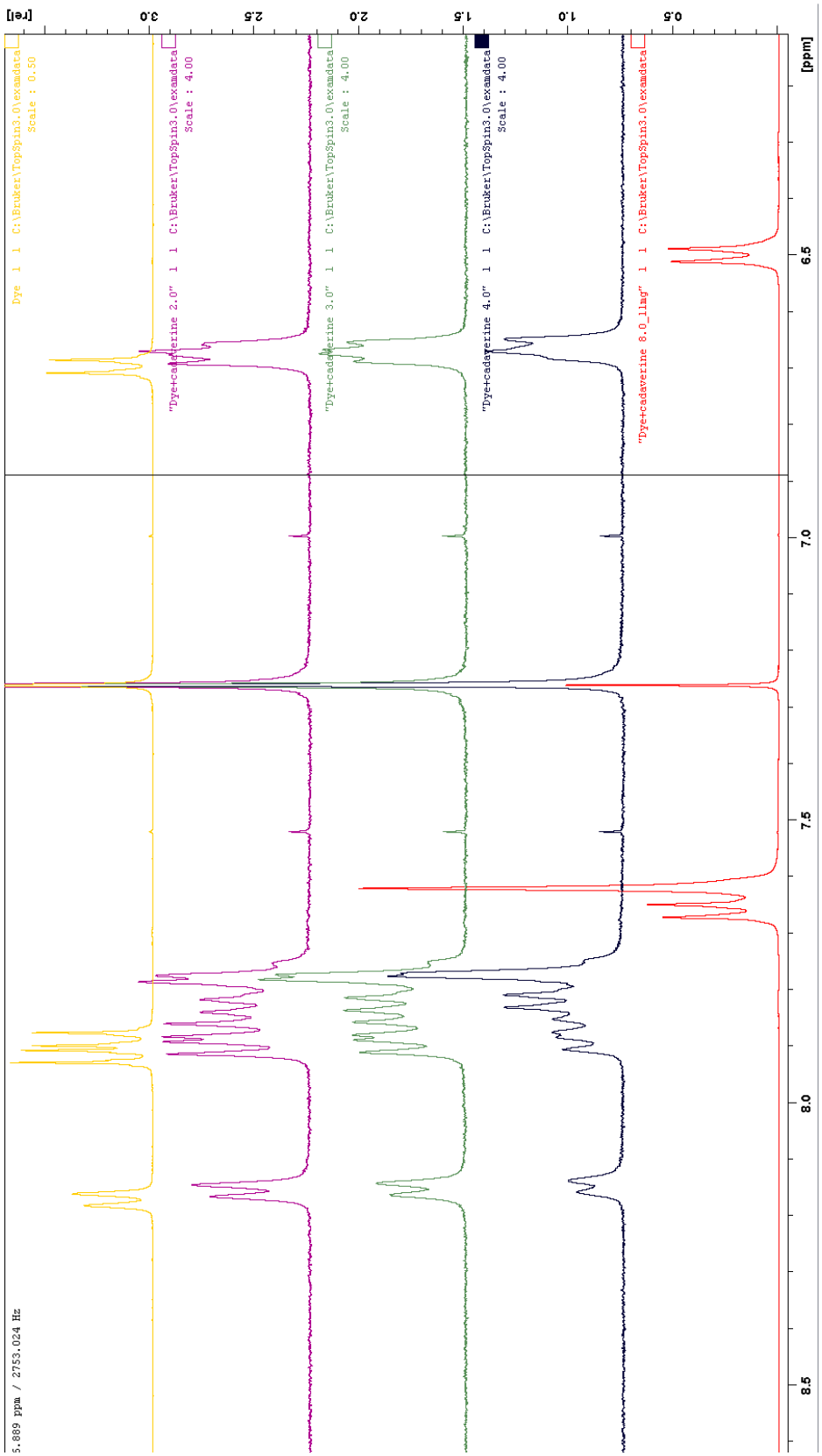
1.9 ^{1}H NMR Spectrum of Dye + cadaverine (1:3 eqv.) (spectrum taken after 20 min)



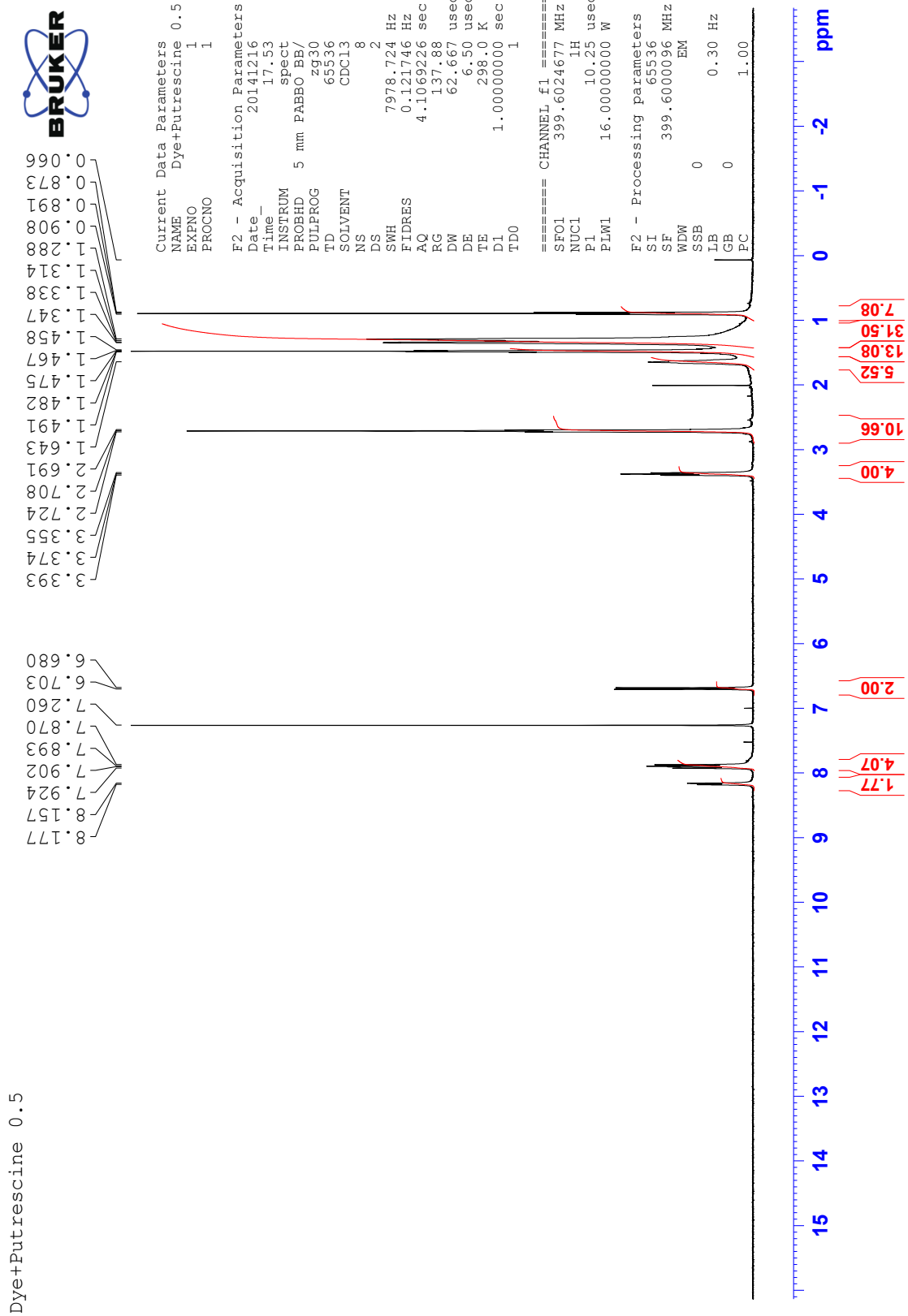
1.10 ^{1}H NMR Spectrum of Dye + cadaverine (1:4 eqv.) (spectrum taken after 20 min)



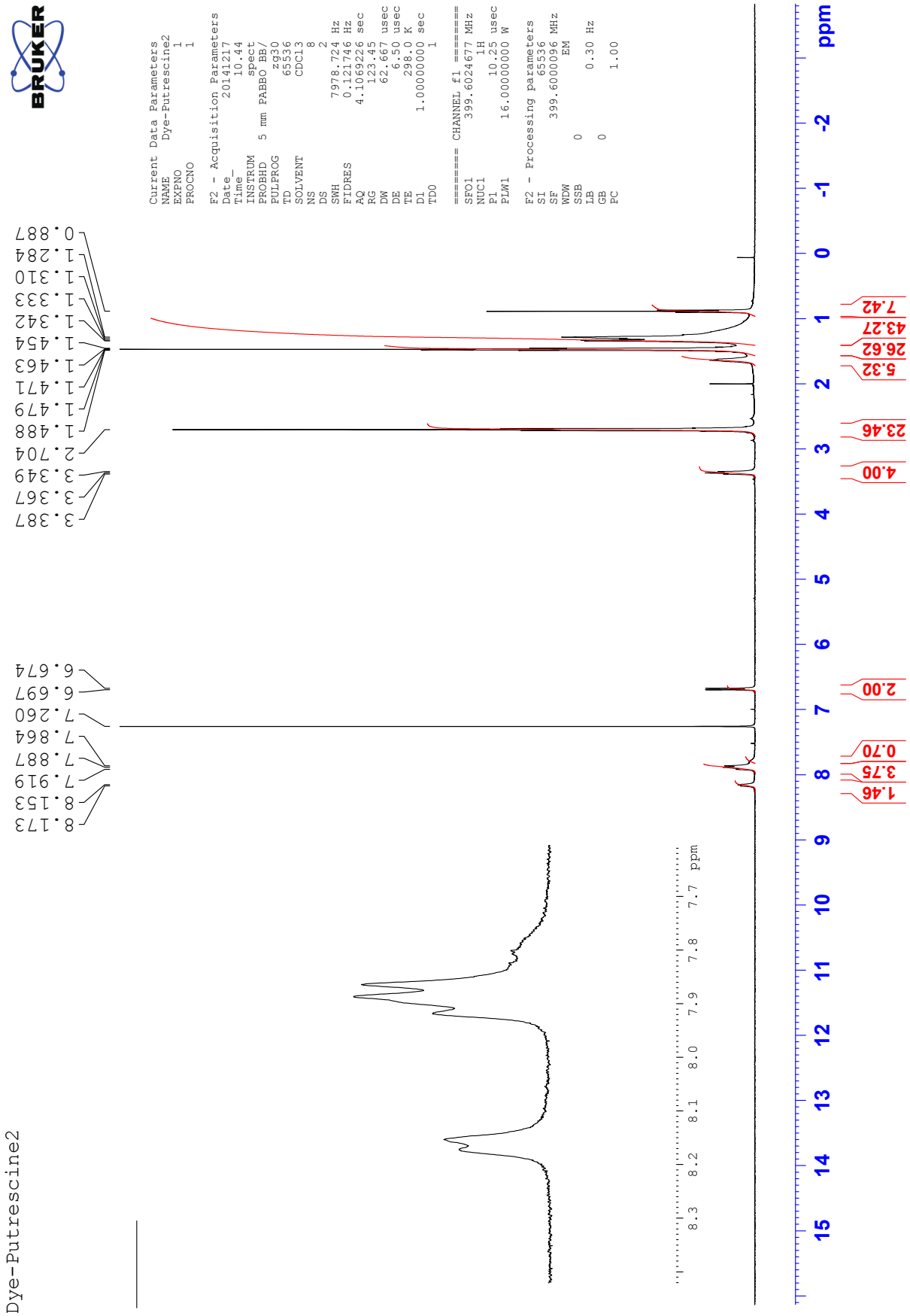
1.11 Comparison of spectra (dye and dye-cadaverine adduct at different concentrations):



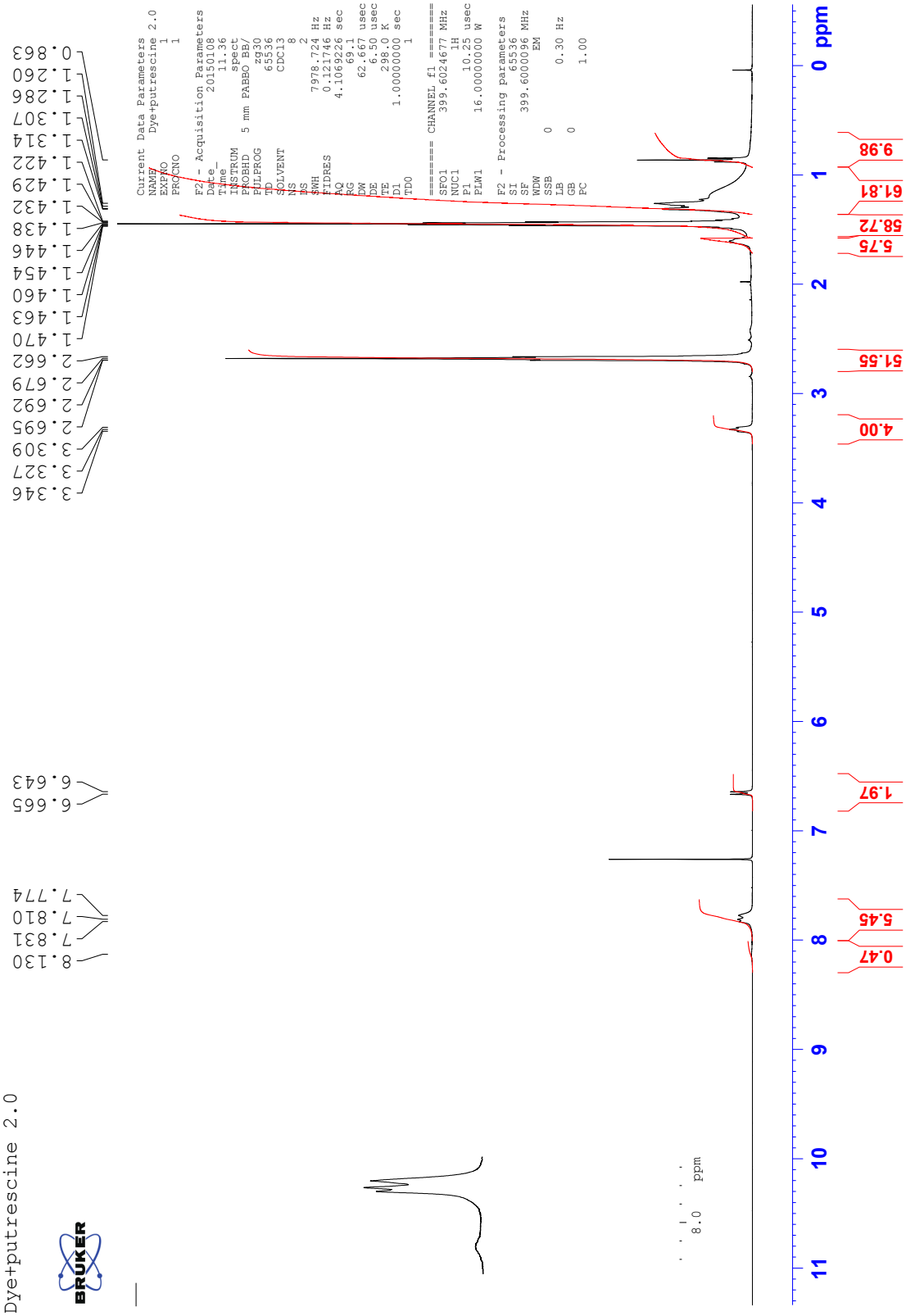
1.12 ^{1}H NMR Spectrum of Dye + Putrescine (1:0.5 eqv.) (spectrum taken after 20 min)



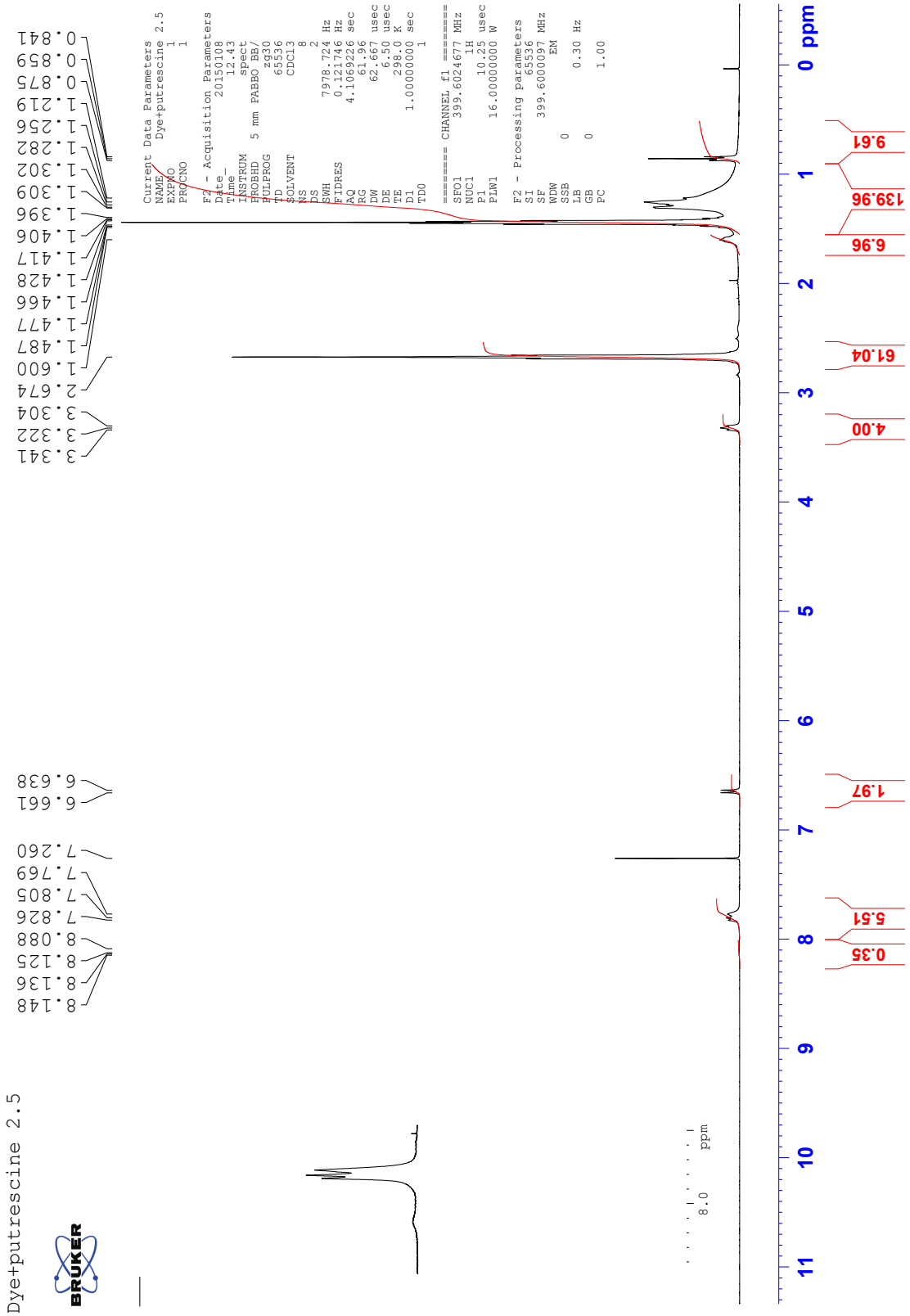
1.13 ^{1}H NMR Spectrum of Dye + Putrescine (1:1 eqv.) (spectrum taken after 20 min)



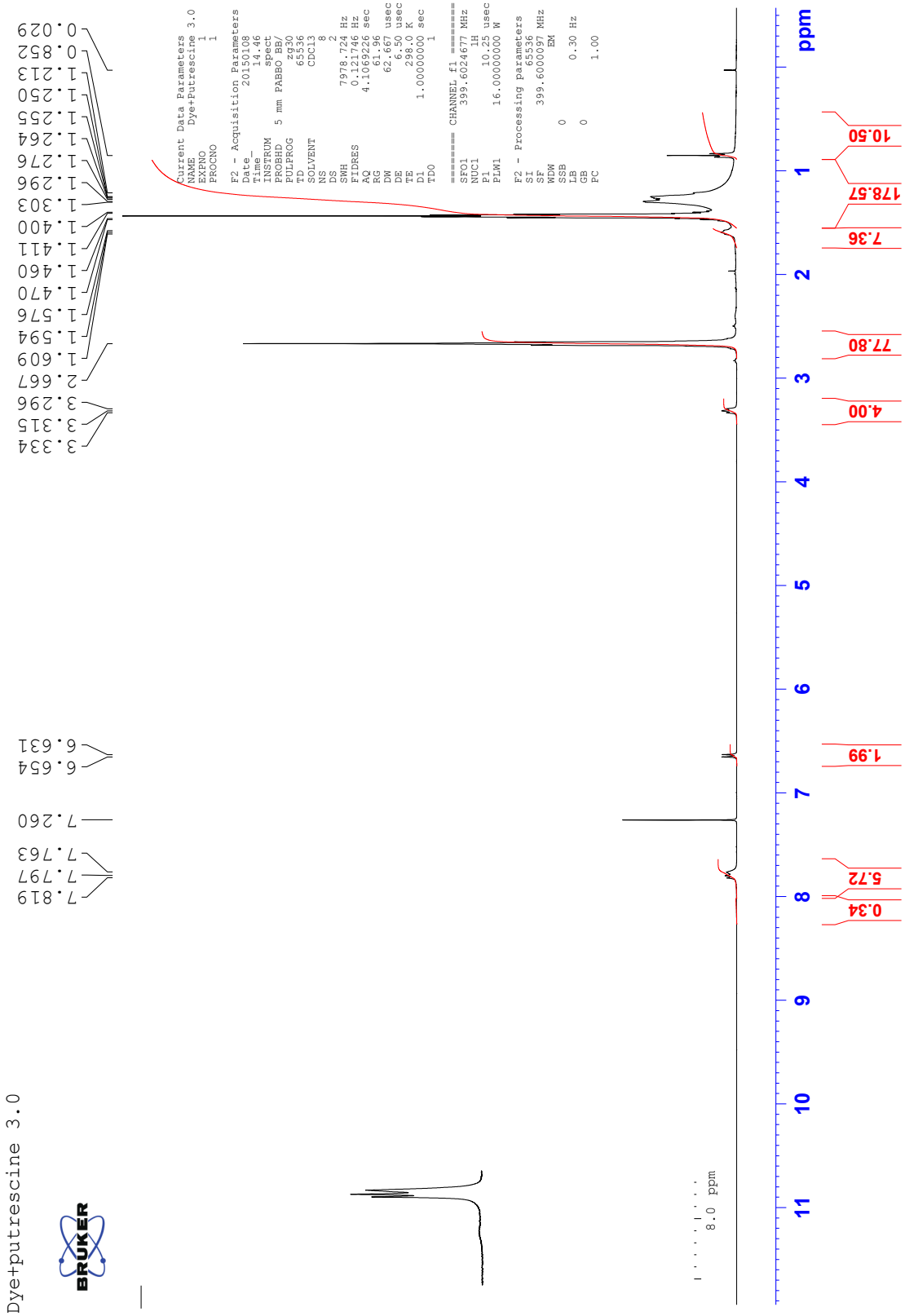
1.14 ^{1}H NMR Spectrum of Dye + Putrescine (1:2 eqv.) (spectrum taken after 20 min)



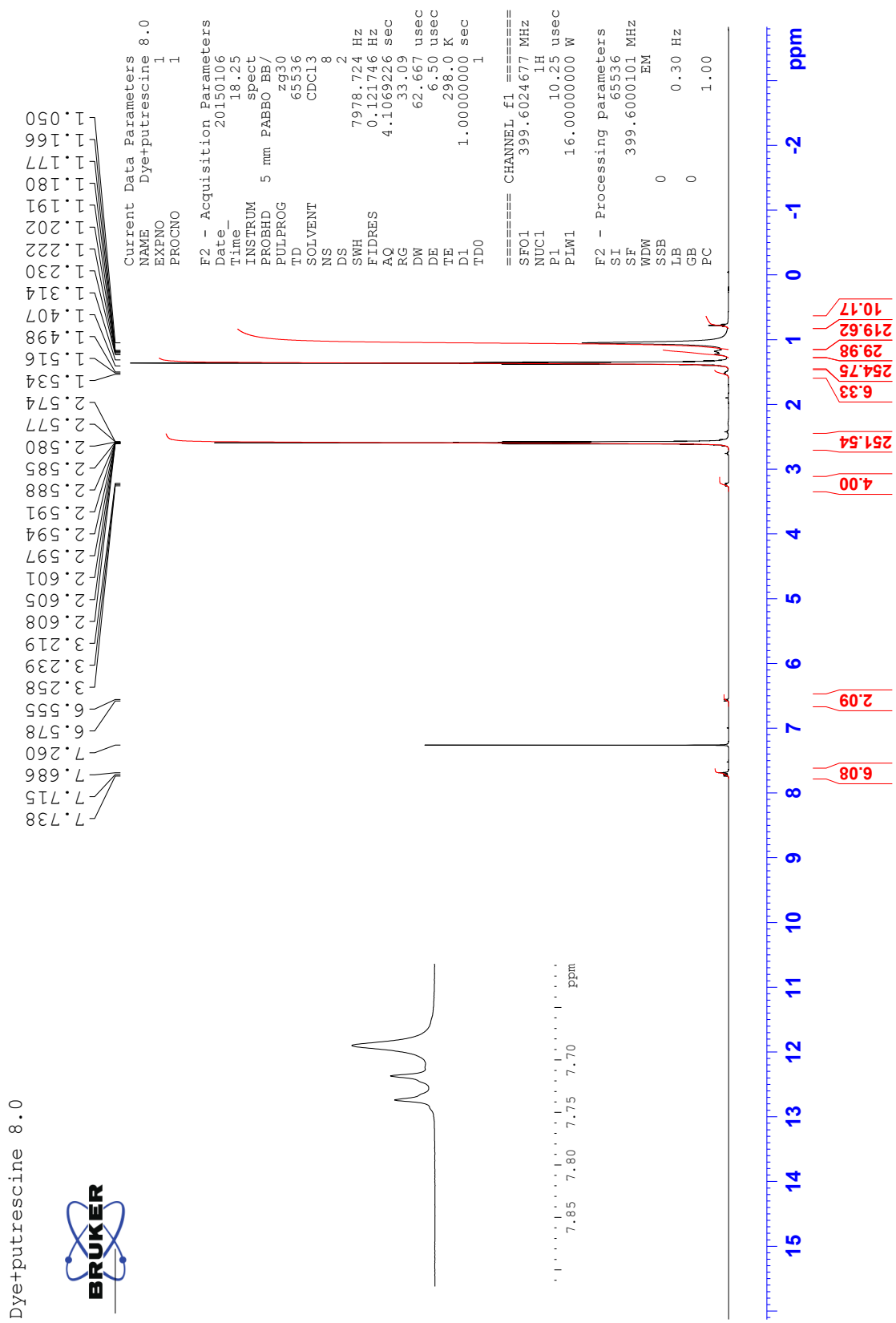
1.15 ^{1}H NMR Spectrum of Dye + Putrescine (1:2.5 eqv.) (spectrum taken after 20 min)



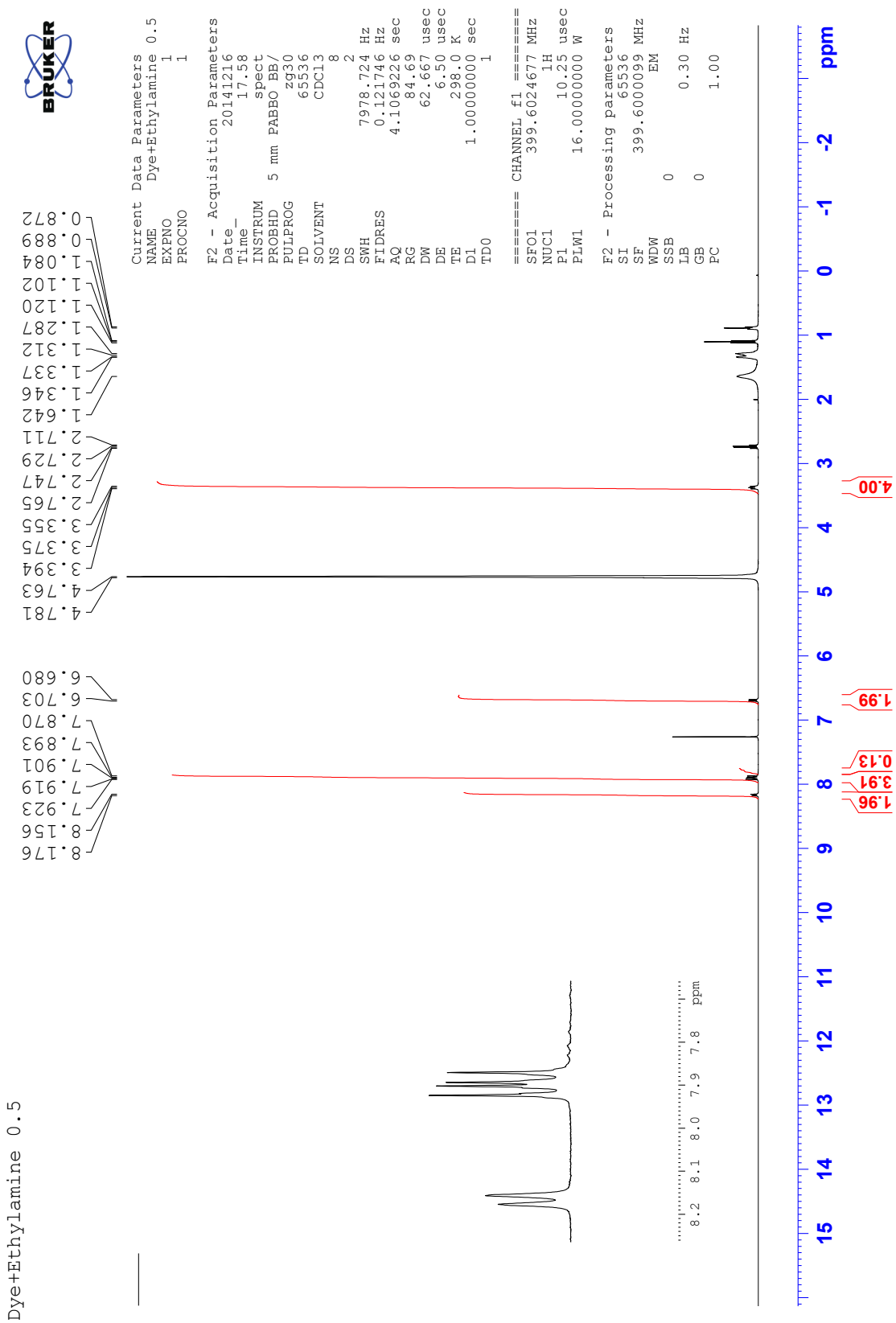
1.16 ^{1}H NMR Spectrum of Dye + Putrescine (1:3 eqv.) (spectrum taken after 20 min)



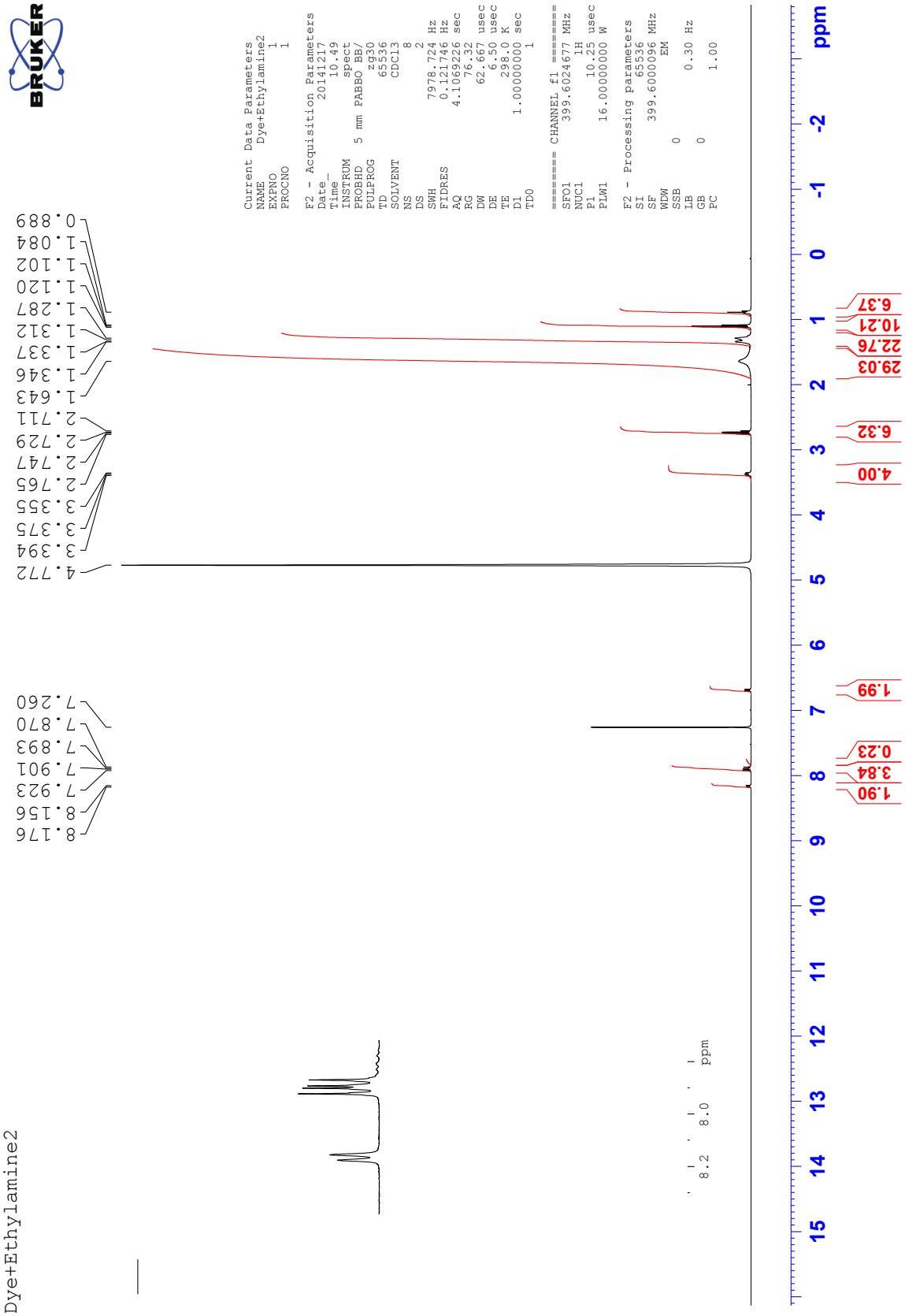
1.17 ^{1}H NMR Spectrum of Dye + Putrescine (1:8 eqv.) (spectrum taken after 20 min)



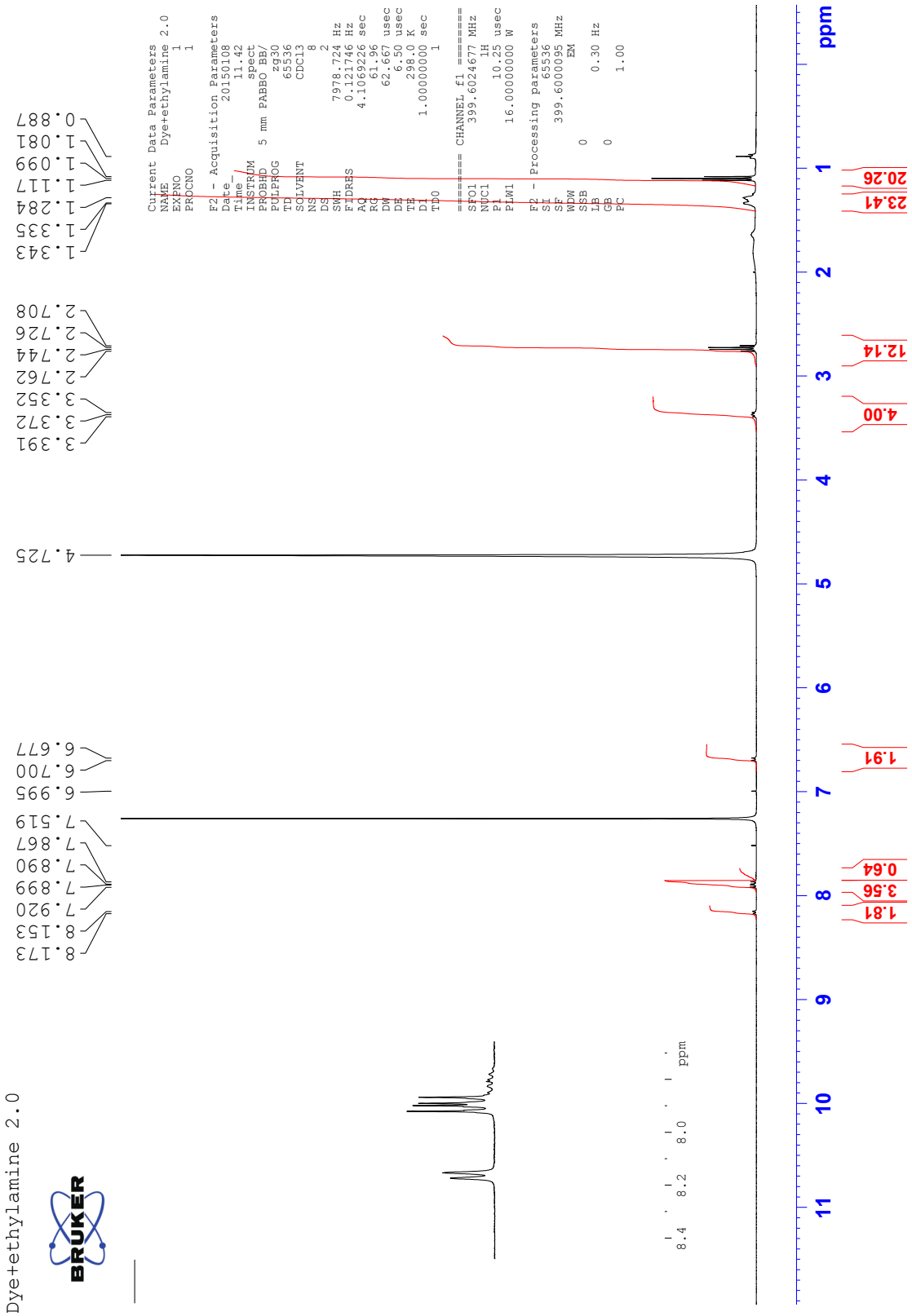
1.18 ^{1}H NMR Spectrum of Dye + Ethylamine (1:0.5 eqv.) (spectrum taken after 20 min).



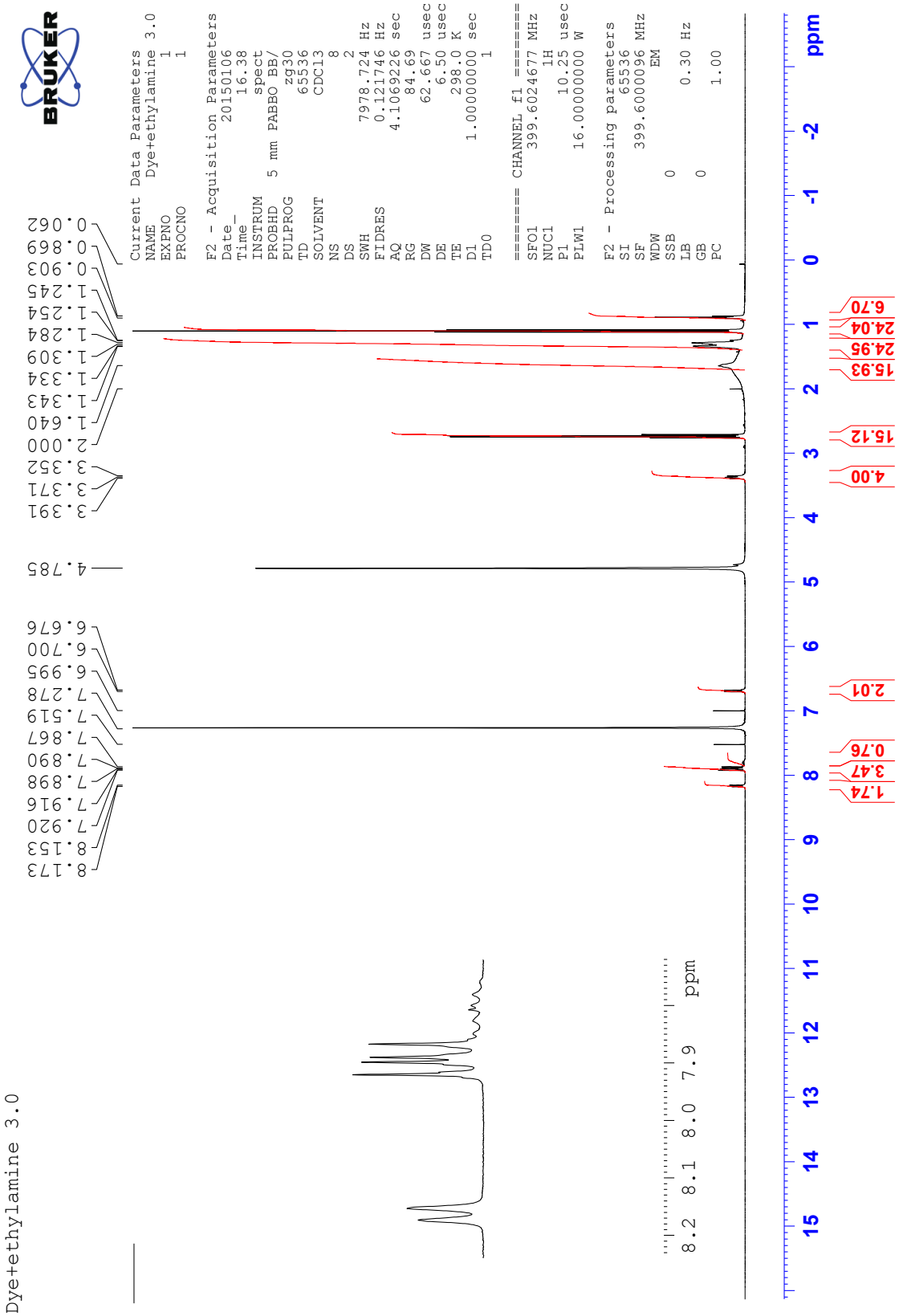
1.19 ^{1}H NMR Spectrum of Dye + Ethylamine (1:1 eqv.) (spectrum taken after 20 min)



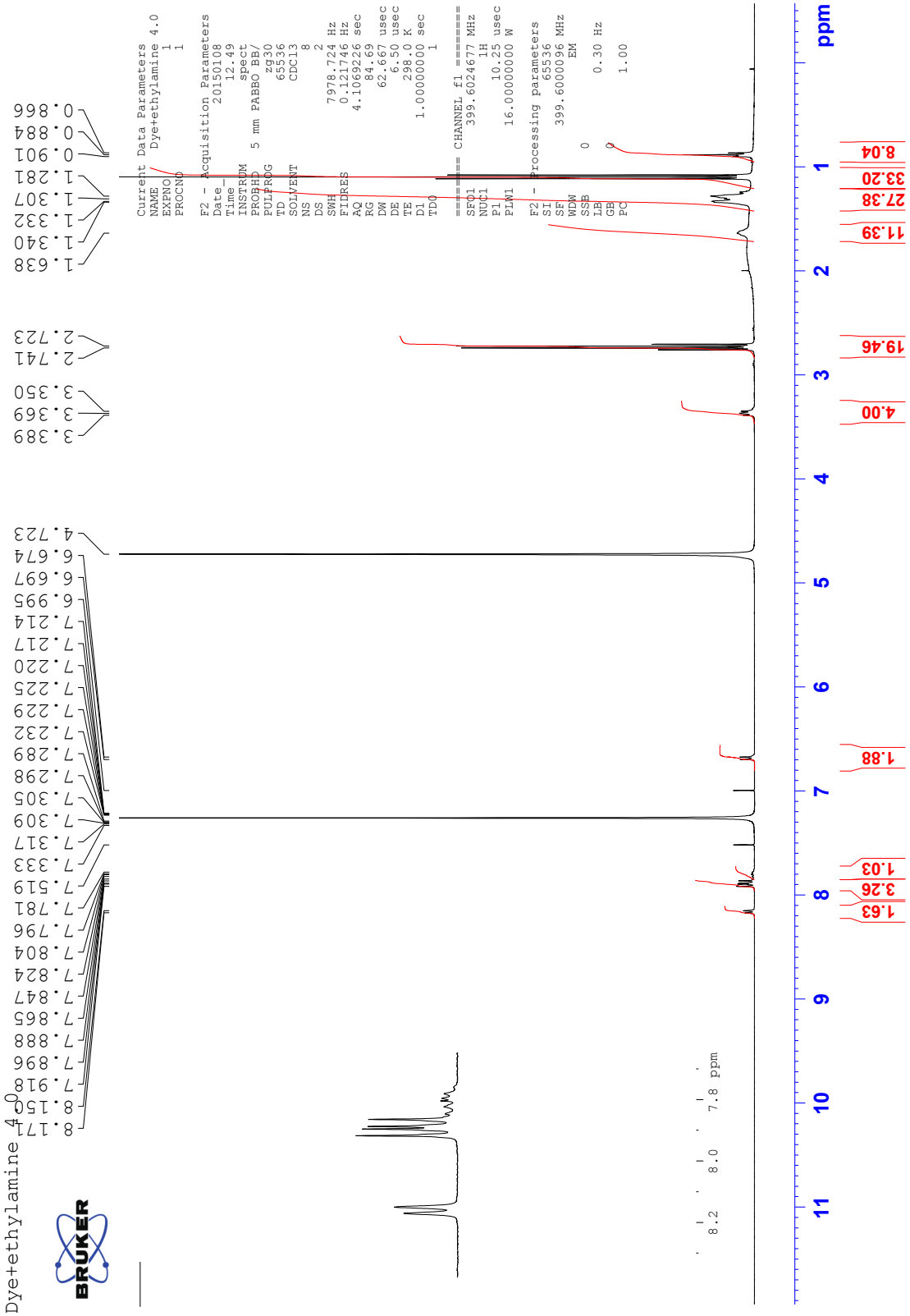
1.20 ^{1}H NMR Spectrum of Dye + Ethylamine (1:2 eqv.) (spectrum taken after 20 min)



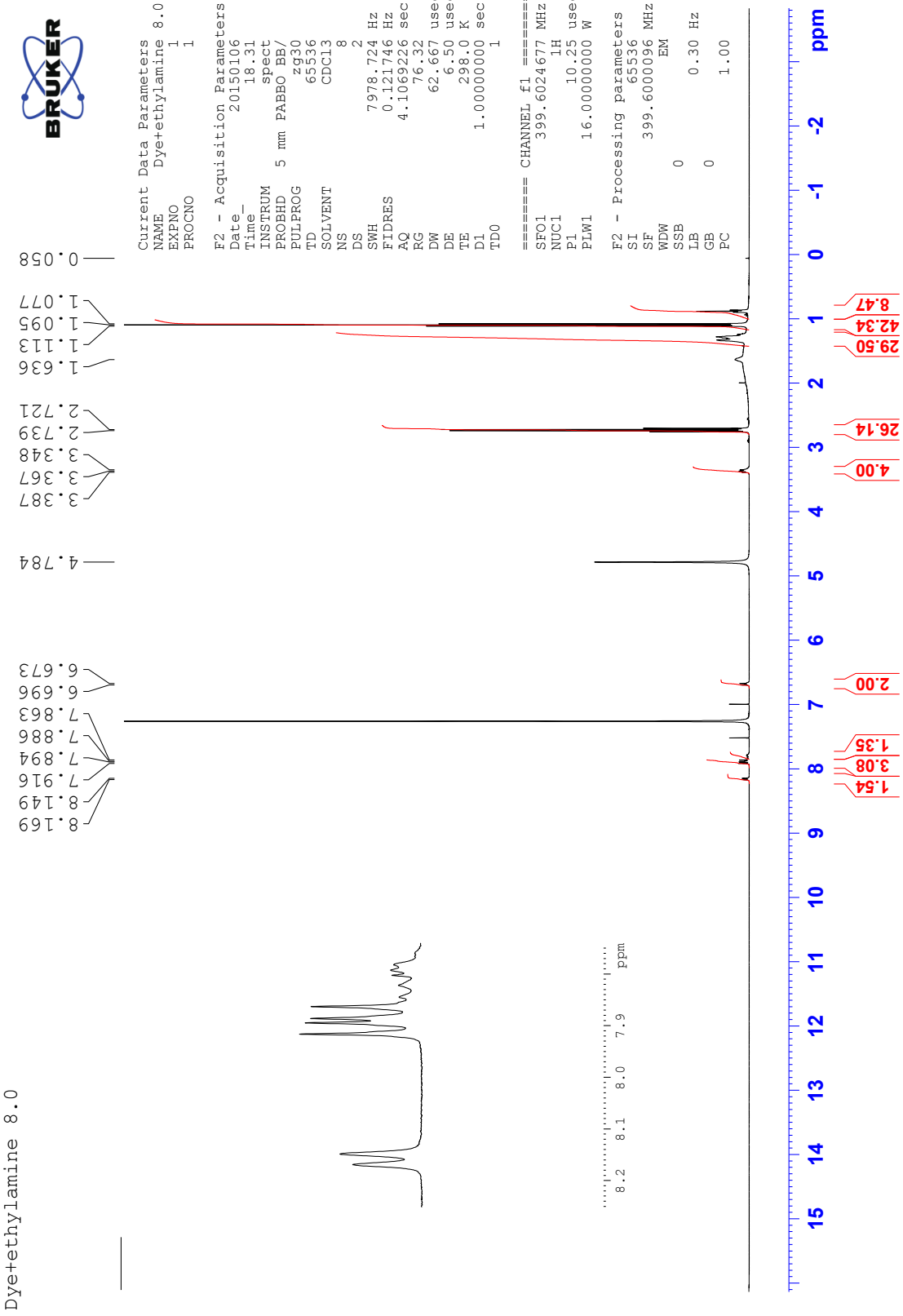
1.21 ^{1}H NMR Spectrum of Dye + Ethylamine (1:3 eqv.) (spectrum taken after 20 min)



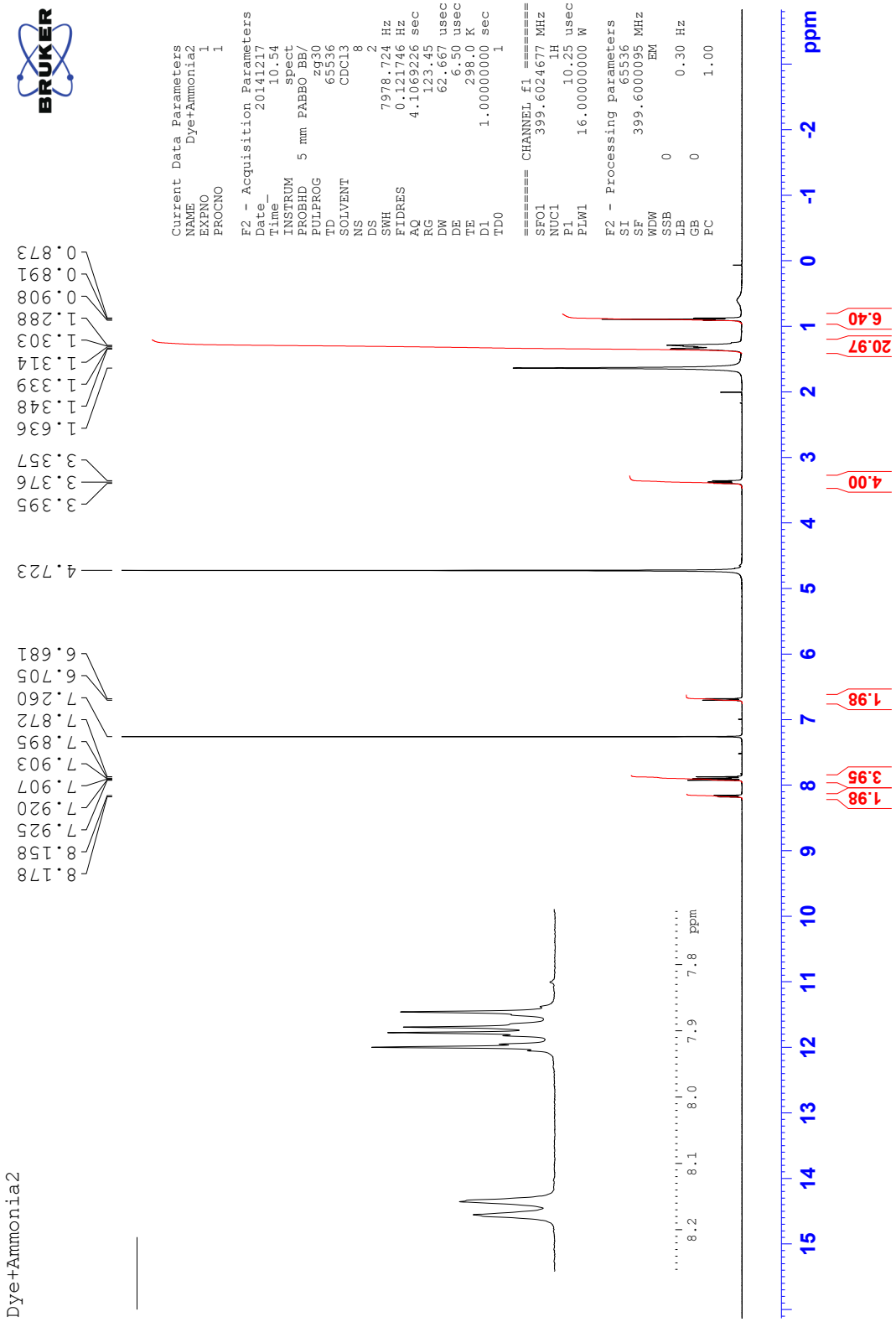
1.22 ^{1}H NMR Spectrum of Dye + Ethylamine (1:4eqv.) (spectrum taken after 20 min)



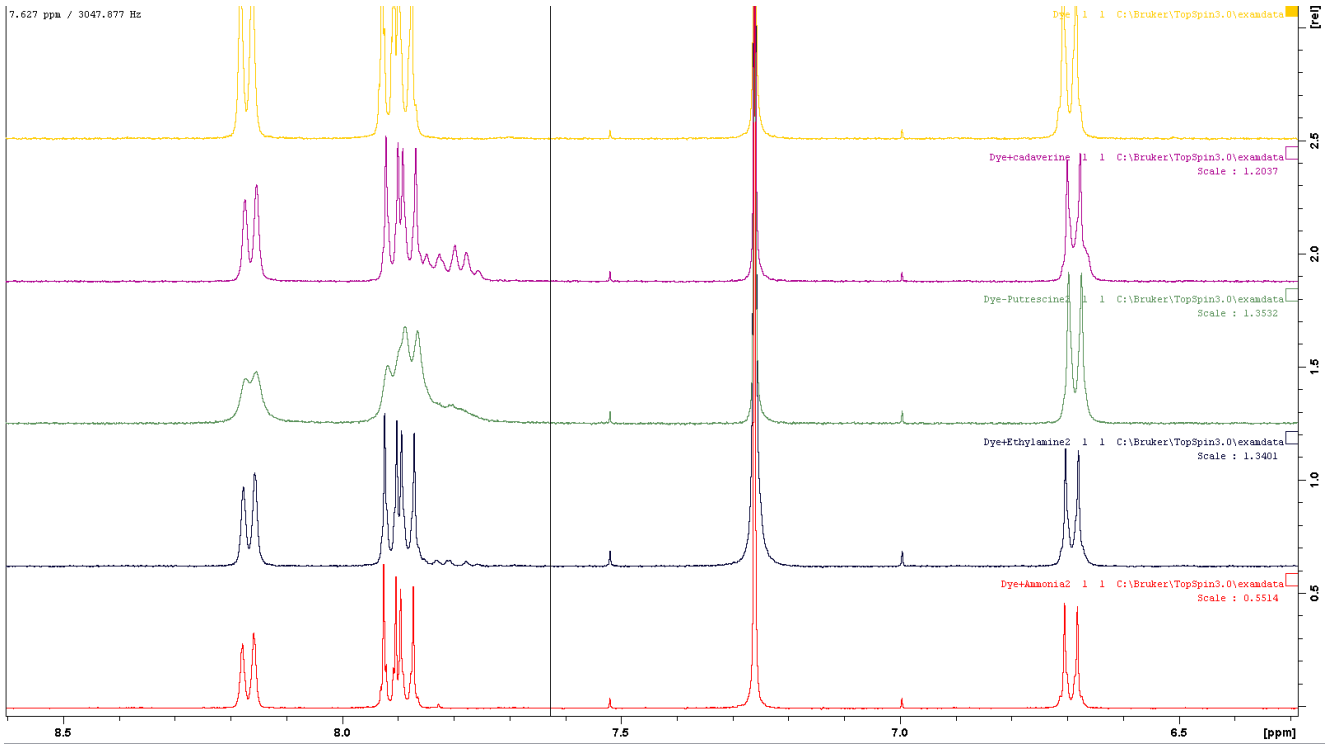
1.23 ^{1}H NMR Spectrum of Dye + Ethylamine (1:8 eqv.) (spectrum taken after 20 min)



1.24 ^{1}H NMR Spectrum of Dye + ammonia (1:1 eqv.) (spectrum taken after 20 min).



1.25 Comparison of spectra



References:

1. Eric Mertz, James B. Beil, and Steven C. Zimmerman *Org. Lett.,* 2003, *5*, 3127-3130
2. Malwina Allen And John D. Roberts *Can. J. Chem*.,1981, *59*. 451-458

Color transformation from RGB to Lab space

Before the image processing, four different color pattern (three reference colors patterns (red, green and blue) and the sensor pattern) are cropped separately. The size of each input color pattern is about 25×25 pixels. Color in RGB space (r, g, b) were converted to CIELAB colorspace (L, a, b) using Matlab functions.

```
cform = makecform('srgb2lab');
lab_image = applycform(rgb_image, cform);
```

The average values for L*, a* and b* were then calculated for every four squares.

```
average_L = lab2double(mean(mean(lab_image(:,:,1))));
average_a = lab2double(mean(mean(lab_image(:,:,2))));
average_b = lab2double(mean(mean(lab_image(:,:,3))));
```

In mathematical form, the color transformation is done by two steps: (1) from sRGB color space to CIEXYZ color space, (2) from CIEXYZ color space to CIELAB color space.

Before the color transformation, the color correction of input images must be taken to eliminate the photographical error from the display on monitor. As a result, the color in sRGB space should be modified to linear RGB space as below.[1]

Note: When images are presented on a monitor, the gamma value of color in sRGB space is 2.0 – 2.5 and it should be transformed to 1.0 (in linear RGB space).

$$C_{linear} = \begin{cases} \dfrac{C_{srgb}}{12.92}, if\ C_{srgb} \le 0.03928 \\ (\dfrac{C_{srgb} + 0.055}{1.055})^{2.4}, if\ C_{srgb} > 0.03928 \end{cases}$$

C_{sRGB} is r, g and b value of each input color in sRGB space.

The color transformation from sRGB color space to CIEXYZ color space is followed by the linear equation:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} 0.4124 & 0.3576 & 0.1805 \\ 0.2126 & 0.7152 & 0.0722 \\ 0.0193 & 0.1192 & 0.9505 \end{bmatrix} \begin{bmatrix} R_{linear} \\ G_{linear} \\ B_{linear} \end{bmatrix}$$

Then, the coordinate of each color (X, Y, Z) in CIEXYZ space was subsequently transformed to (L, a, b) in Lab color space.[2]

$$L = 116 \times f\left(\frac{Y}{Y_n}\right) - 16$$

$$a = 500 \times \left[f\left(\frac{X}{X_n}\right) - f\left(\frac{Y}{Y_n}\right)\right]$$

$$b = 200 \times \left[f\left(\frac{Y}{Y_n}\right) - f\left(\frac{Z}{Z_n}\right)\right]$$

$$f(I) = \begin{cases} I^{1/3}, & if\ I > (6/29)^3 \\ \left(\frac{841}{108}\right) I + \frac{4}{29}, & if I \leq (6/29)^3 \end{cases}$$

Where (X_n, Y_n, Z_n) is coordinate of the white point in CIEXYZ space (in our calculation, it is (0.9504, 1.0000, 1.0889) for the definition of white point in CIE Standard Illuminant D65).

[1] M. Stokes, M. Anderson, S. Chandrasekar, R. Motta, *A Standard Default Color Space for the Internet – sRGB, Version 1.10,* 1996.

[2] J. Schanda, *Colorimetry: Understanding the CIE system* 2007, 61.

Chemical selectivity and cross-sensitivity of the electrochemical sensors

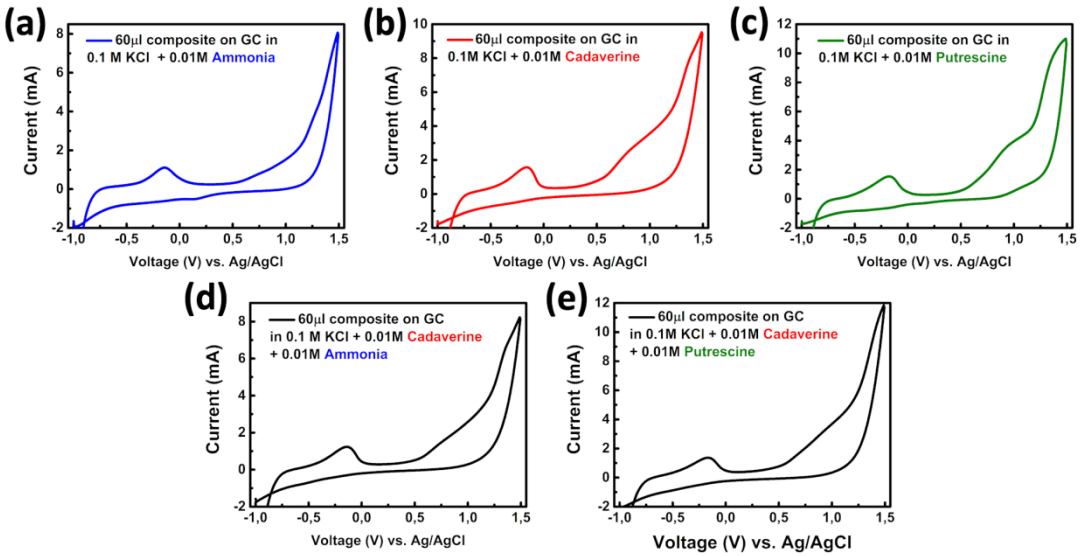


Figure S1 Cyclic voltammetry curves measured with the composite electrodes using electrolytes consisting of only one (a)-(c) or two different types of amines (d) and (e) in the presence of KCl.