Supporting Information

A Real-Time Colorimetric and Ratiometric Fluorescent Probe for Sulfite

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Content:

1. Quantum Yields.

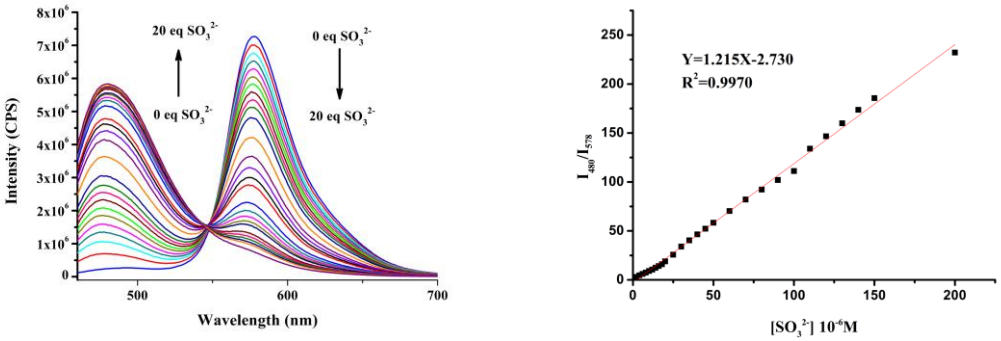
Quantum yields were determined using fluorescein as a standard according to the published method.[1] The quantum yield was calculated according to the equation: ($\Phi_{sample} = \Phi_{standard} * (I_{sample} / I_{standard}) * (A_{sample} / A_{standard})$); where Φ is the quantum yield, $\Phi_{standard}$ = 0.85 in 0.1 M NaOH; I_{sample} and $I_{standard}$ are the integrated fluorescence intensities of the sample and the standard, A_{sample} and $A_{standard}$ are the optical densities, at the excitation wavelength, of the sample and the standard, respectively.

Quantum yield of Probe **1**: Φ = 0.028. Quantum yield of Probe **2**: Φ = 0.089

After the complete reaction with sulfite, the Quantum yield of Probe **1**: Φ = 0.006 Quantum yield of Probe **3**: Φ = 0.006

2. Detection limit.

The detection limit was calculated based on the fluorescence titration.[2] Probe 1 was employed at 10 μM and the slit was adjusted to 5 nm/5 nm. To determine the S/N ratio, the emission intensity of Probe 1 without Na_2SO_3 was measured by 10 times and thestandard deviation of blank measurements was determined. Under the present conditions, a good linear relationship between the fluorescence intensity and the Na_2S concentration could be obtained in the 0 – 200 μM (R = 0.997), as shown in Fig. S1. The detection limit is then calculated with the equation: detection limit = $3\sigma_{bi}/m$, where σ_{bi} is the standard deviation of blank measurements, m is the slope between intensity versus sample concentration. The detection limit was measured to be 58 μM at S/N = 3 (signal-to-noise ratio of 3:1).



A **B**

Fig. S1

A) Fluorescence response of Probe **1** (10 μM) to SO_3^{2-} (0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 200μM, 0-20 eq) (λ_{ex} = 446 nm. Slit: 5 nm/5 nm, λ_{scan} = 460 – 700 nm) in DMF:buffer = 2:8.

B) Fluorescence intensity ratio at 480 nm and 578 nm (I_{480}/I_{578}) of Probe 1 (10 μM) upon addition of SO_3^{2-} (0–200 μM, 0-20 eq) (λ_{ex} = 446 nm. Slit: 5 nm/5 nm) in DMF:buffer = 2:8.

3. **The liner relationship of the fluorescent signal ratio to the concentration of sulfite**

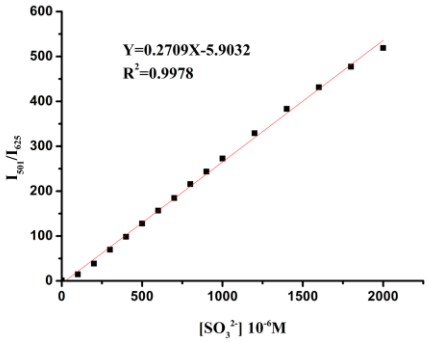


Fig. S2 Fluorescence intensity ratio at 501 nm and 625nm (I_{501}/I_{625}) of Probe 2 (10 μM) upon addition of SO_3^{2-} (0–2000 μM, 0-200 eq) (λ_{ex} = 468 nm. Slit: 3 nm/3 nm) in DMF: buffer = 5:5.

4. The fluorescent emission spectrum of probe 1 with $S_2O_4^{2-}$ and $S_2O_5^{2-}$

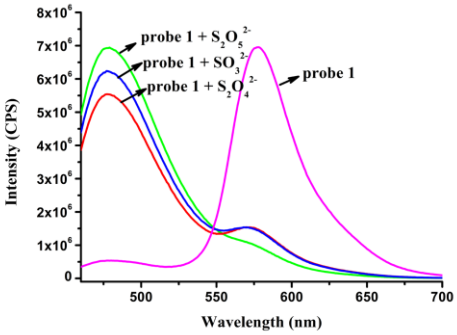
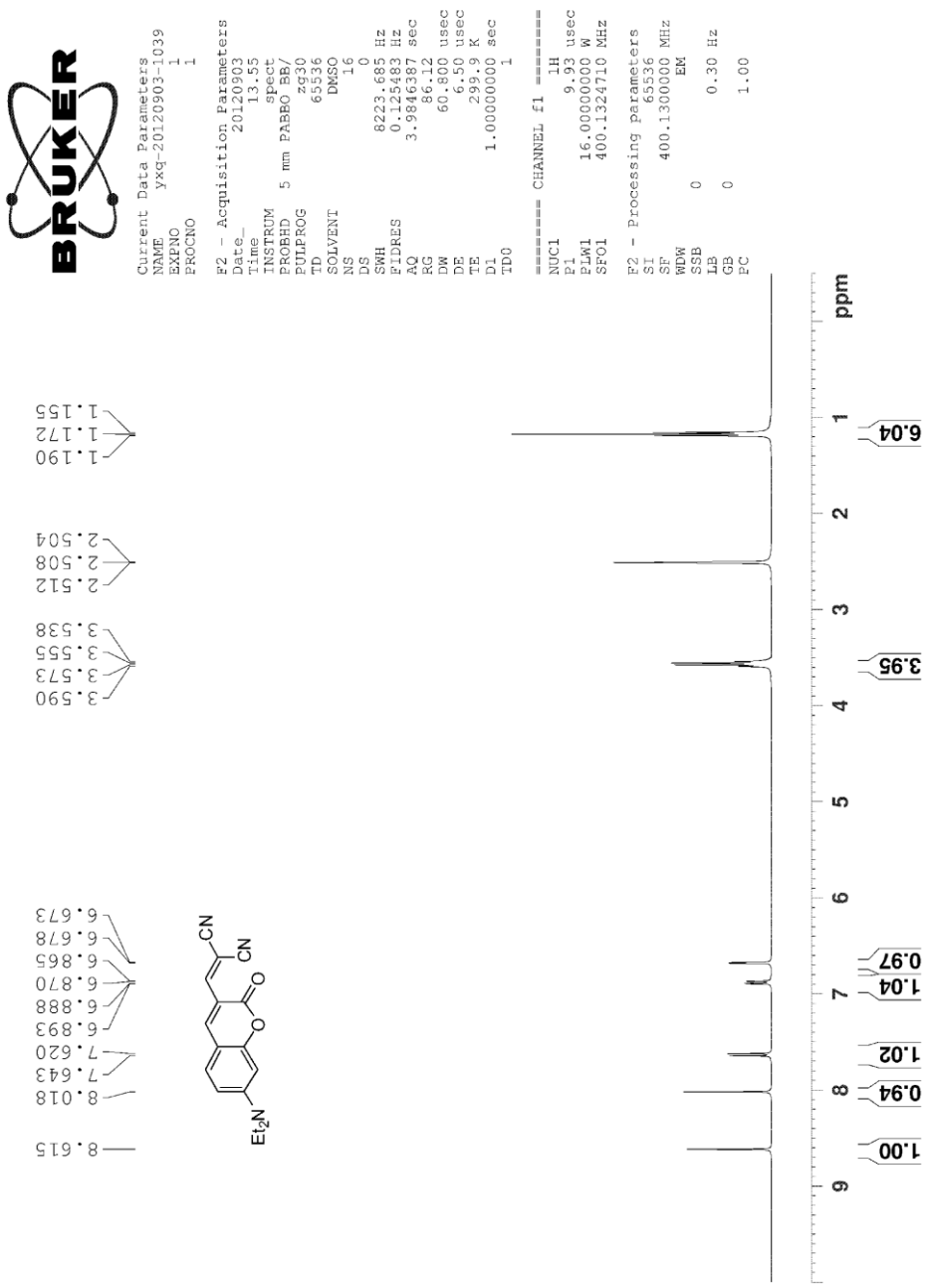
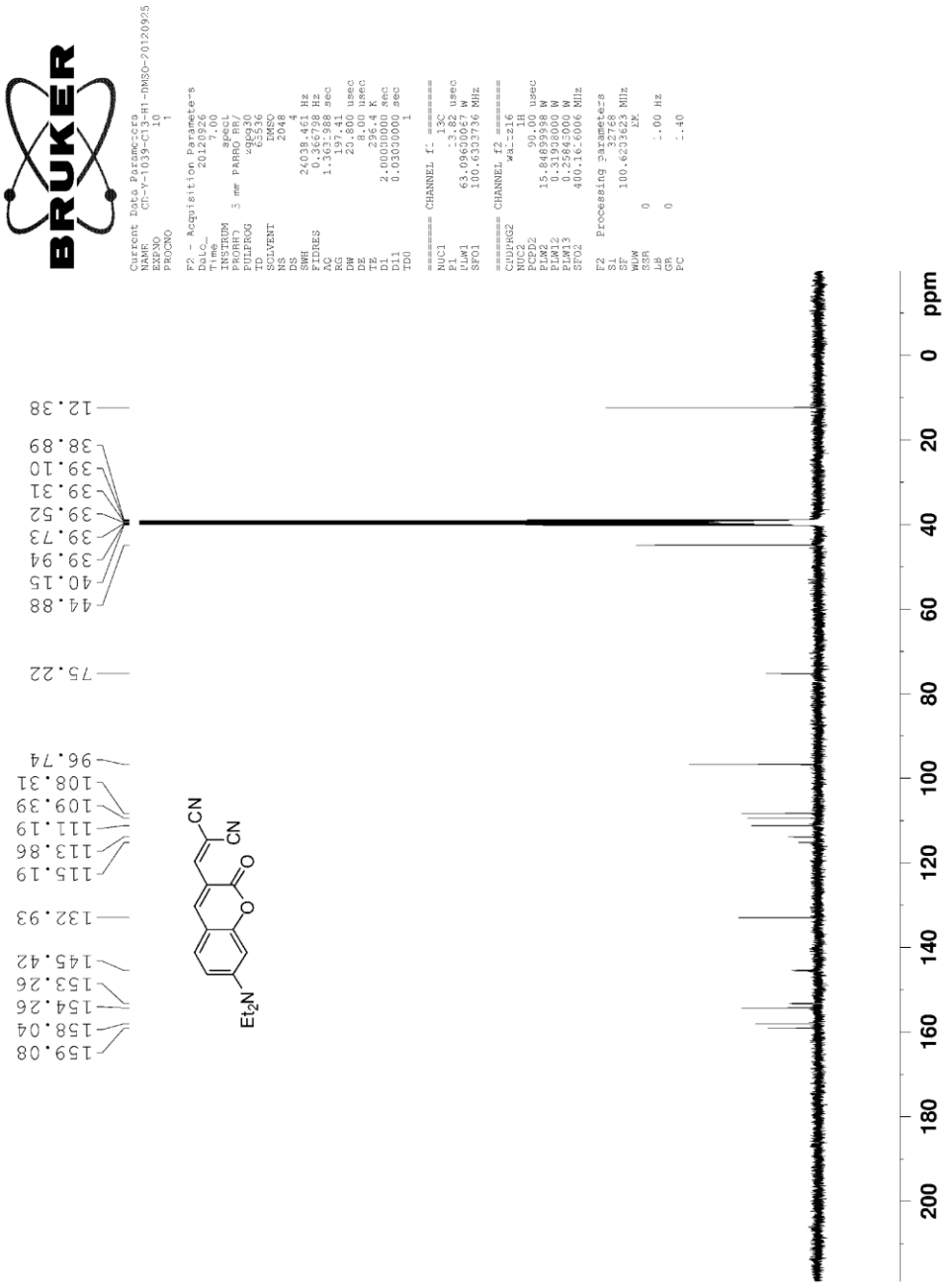


Fig S3

^{1}H NMR and ^{13}C NMR spectrums.

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154.26
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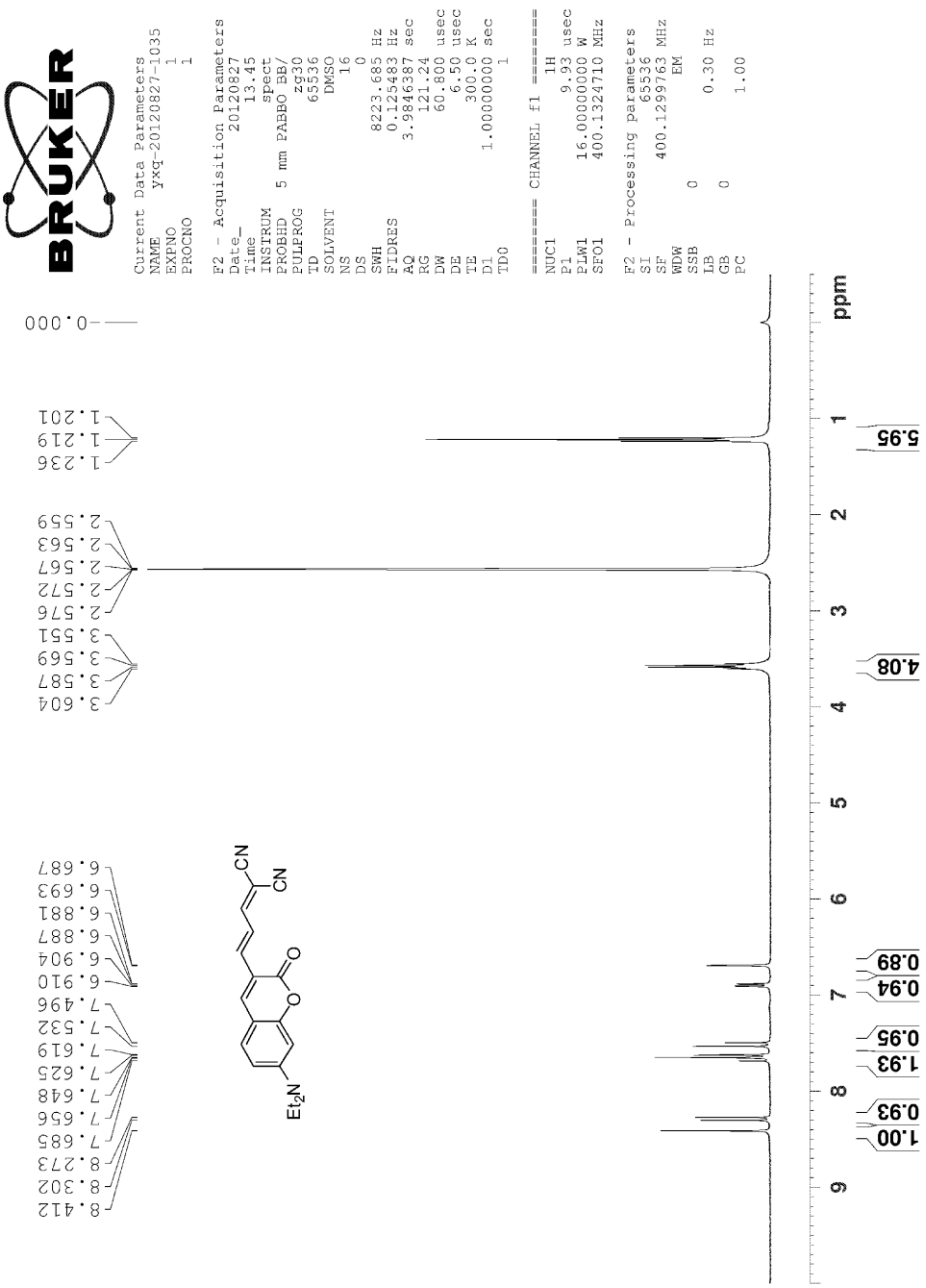
ppm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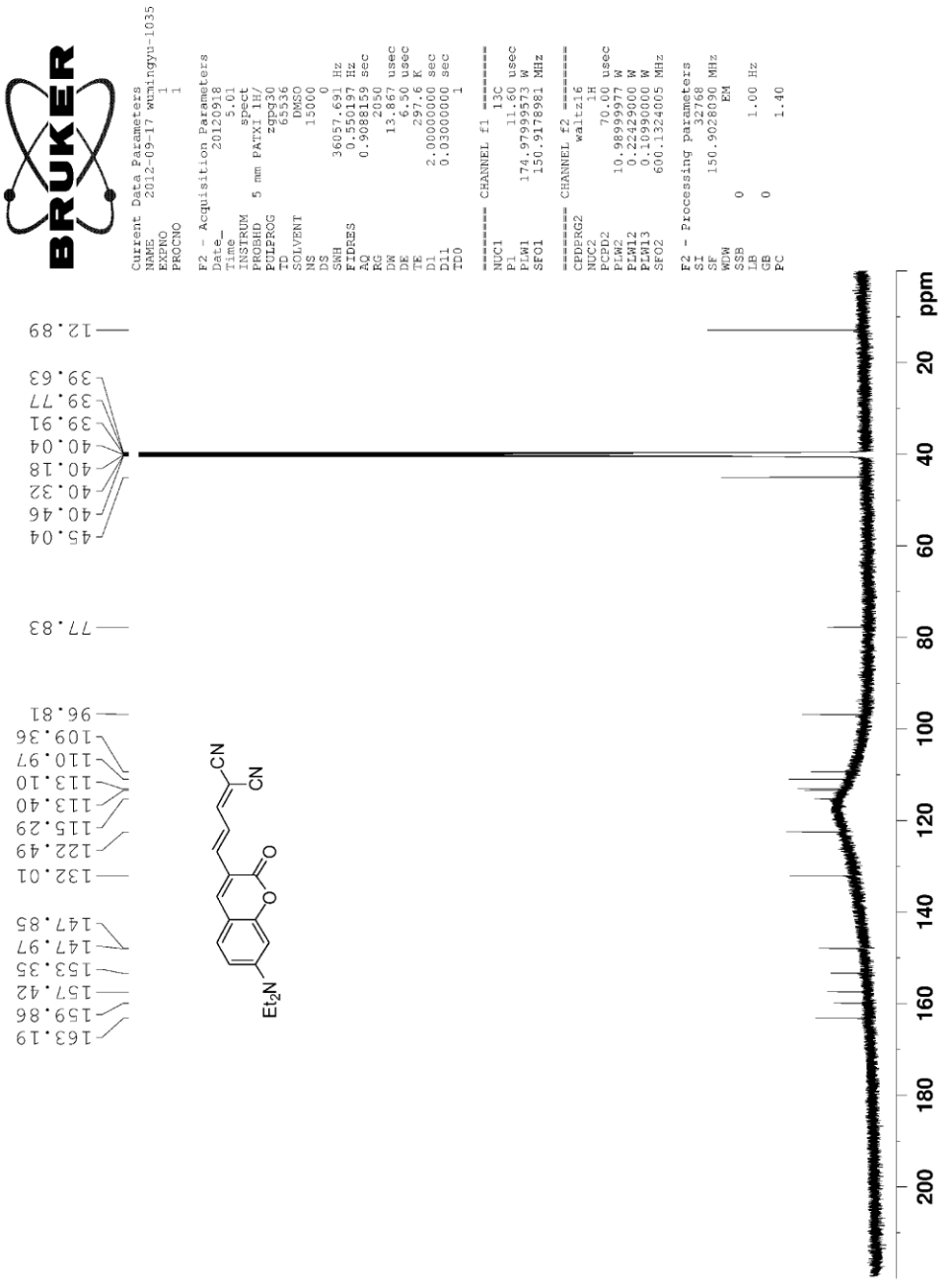
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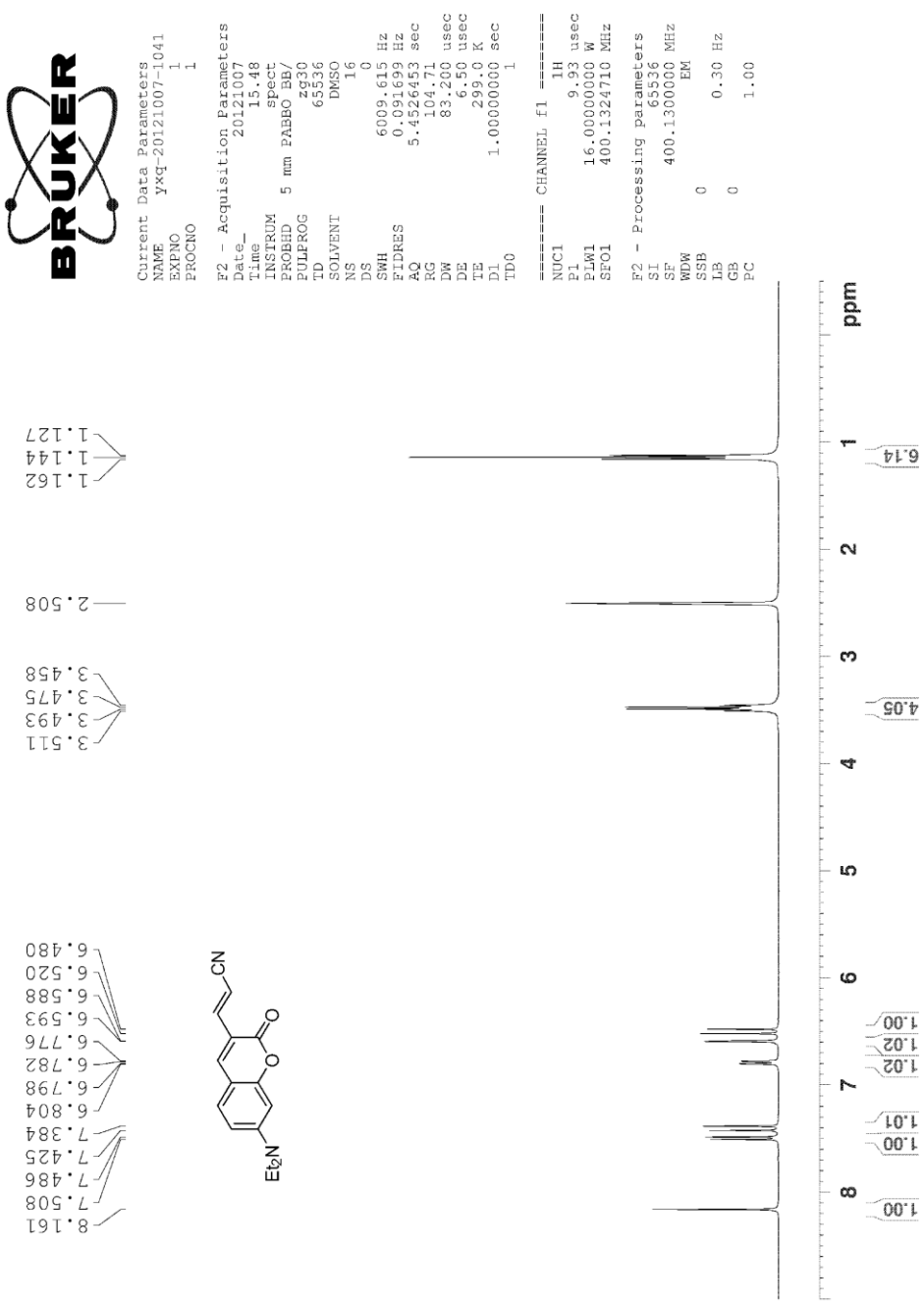
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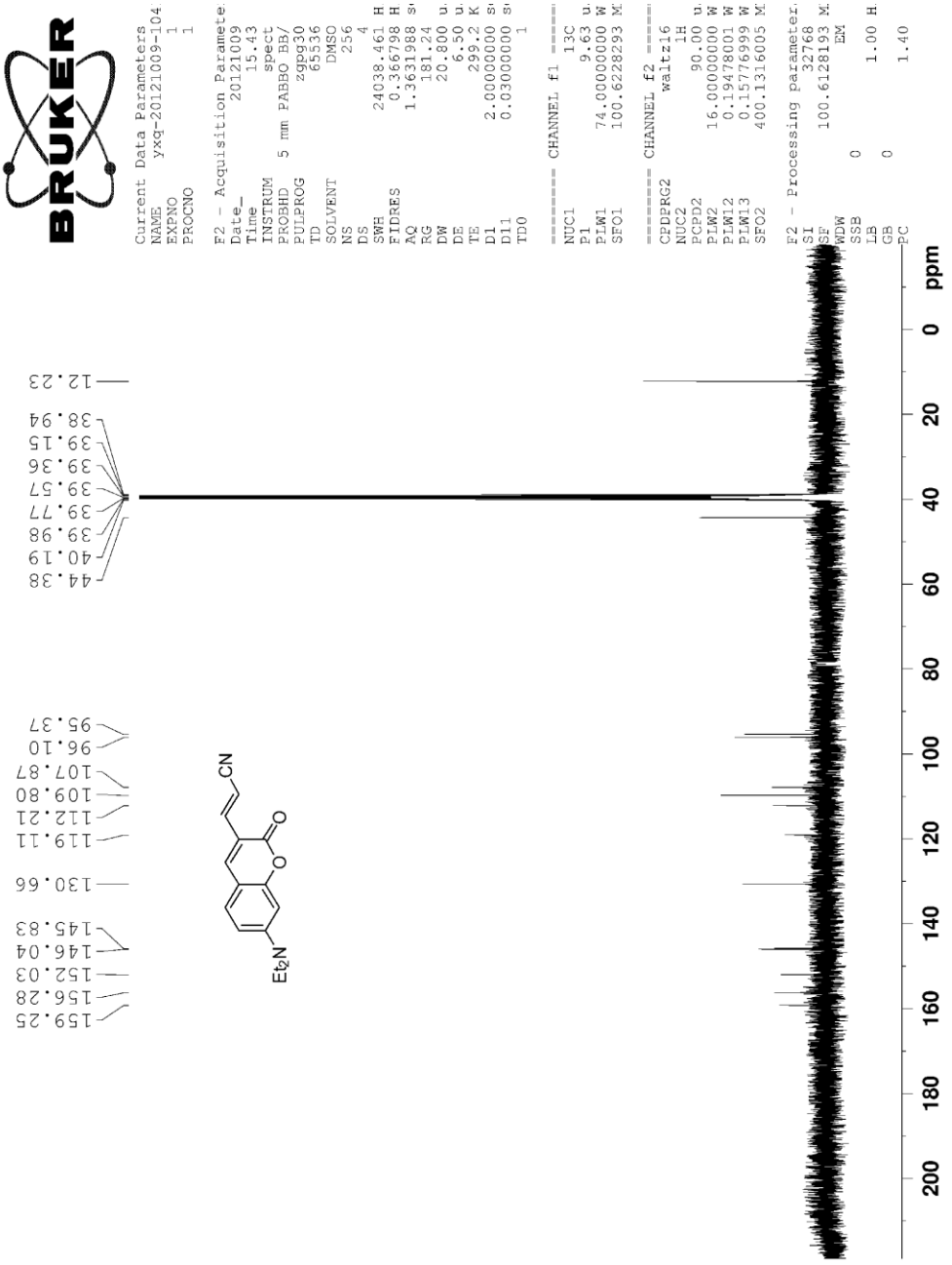
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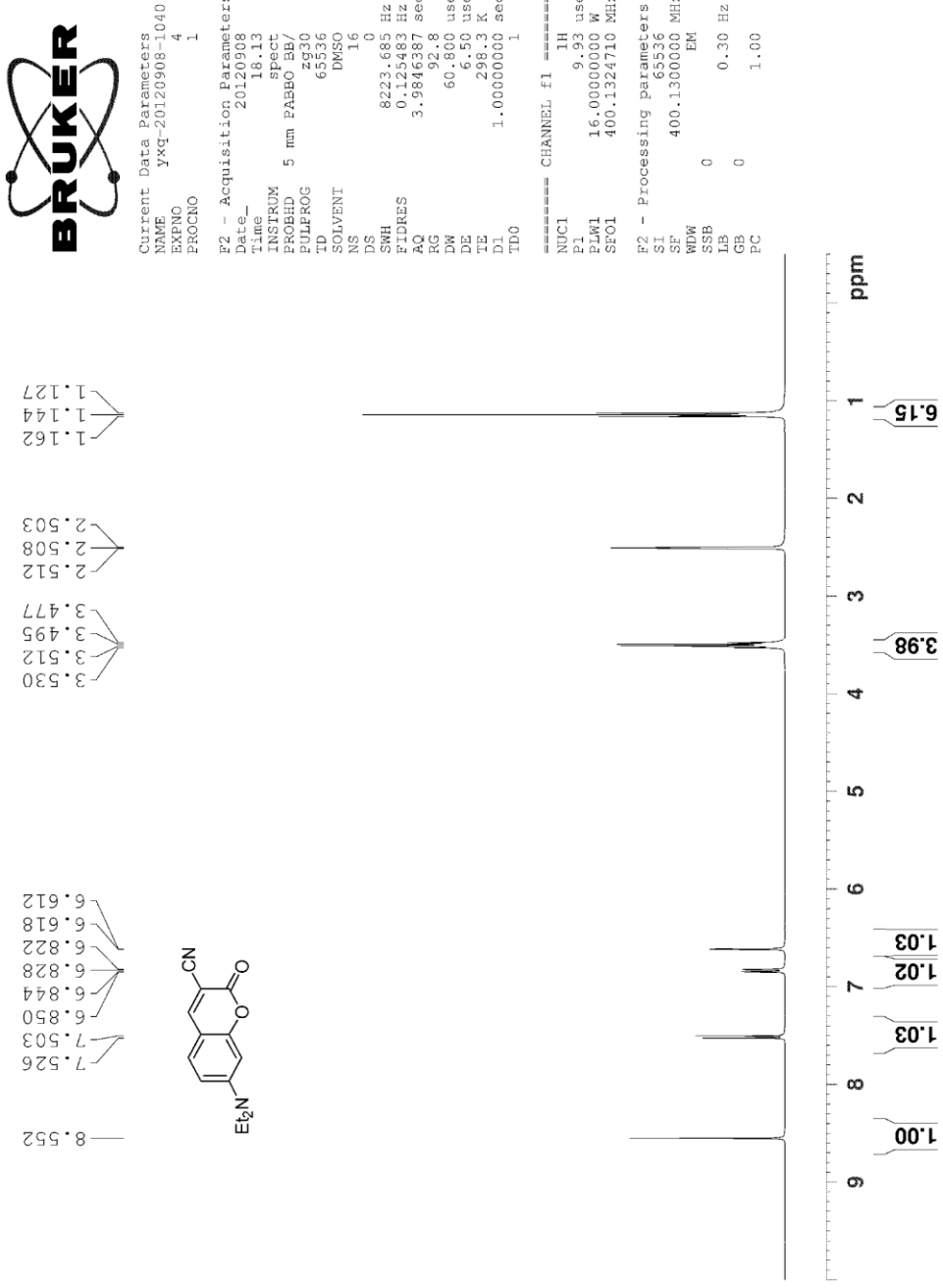
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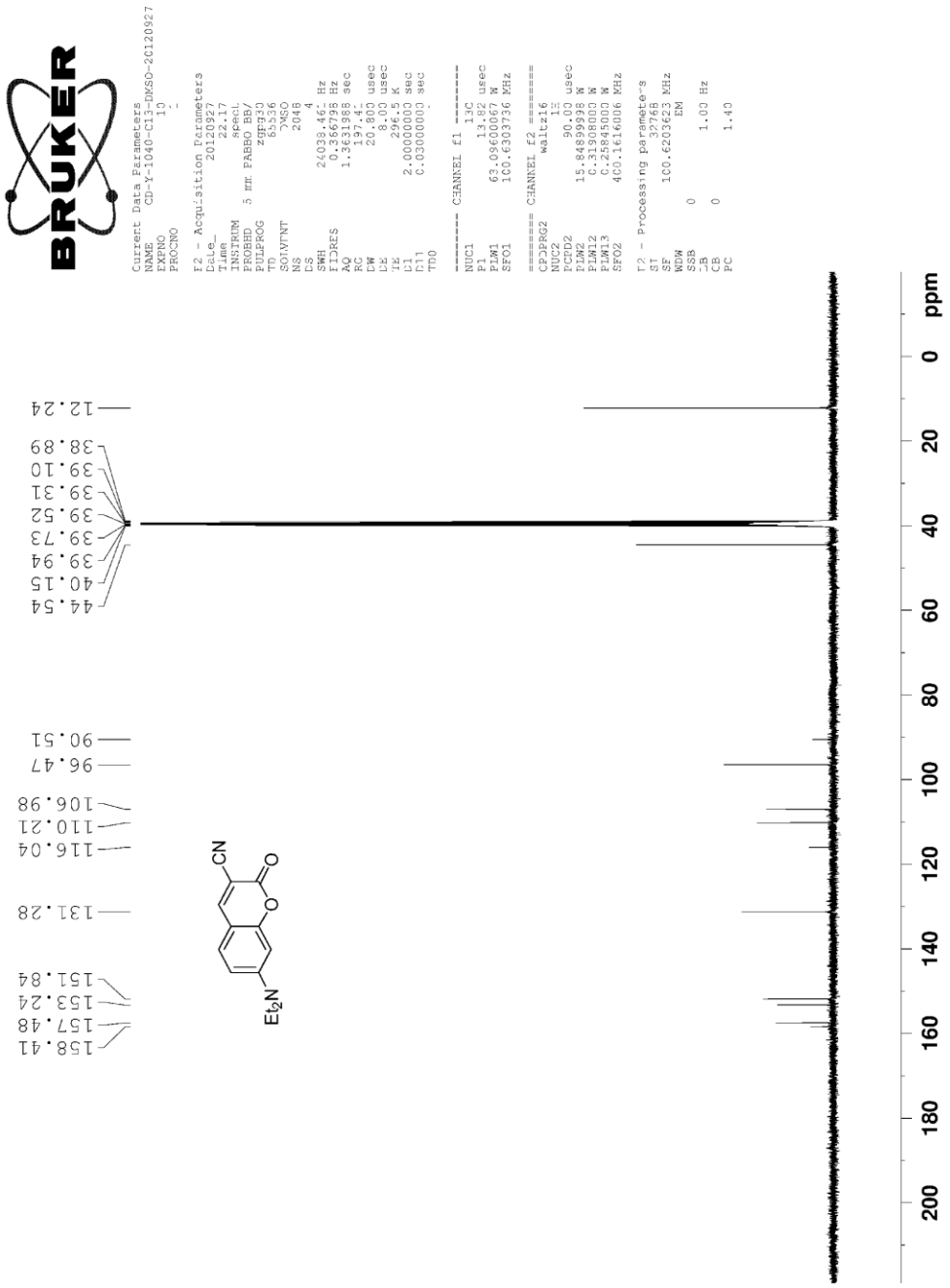
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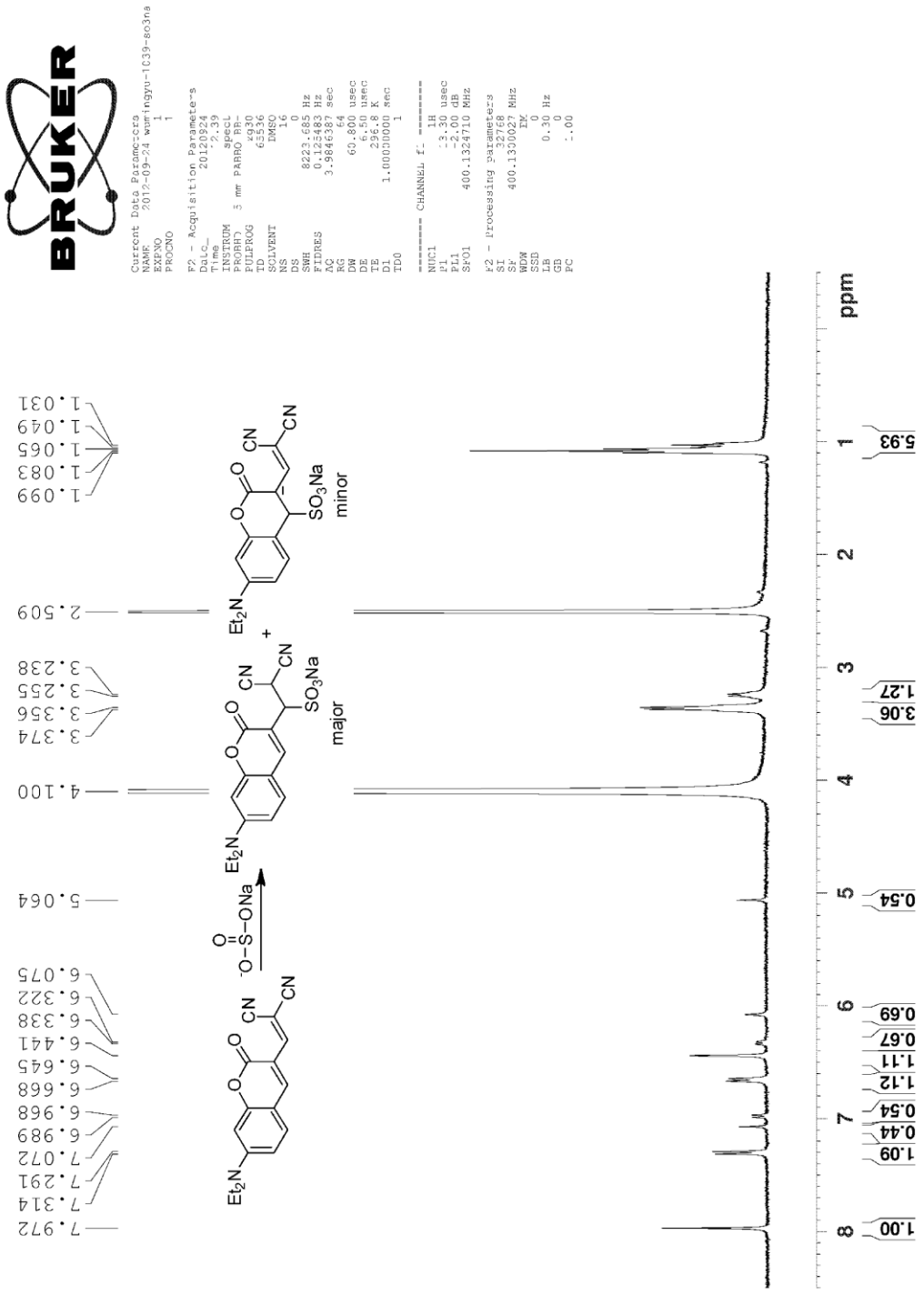
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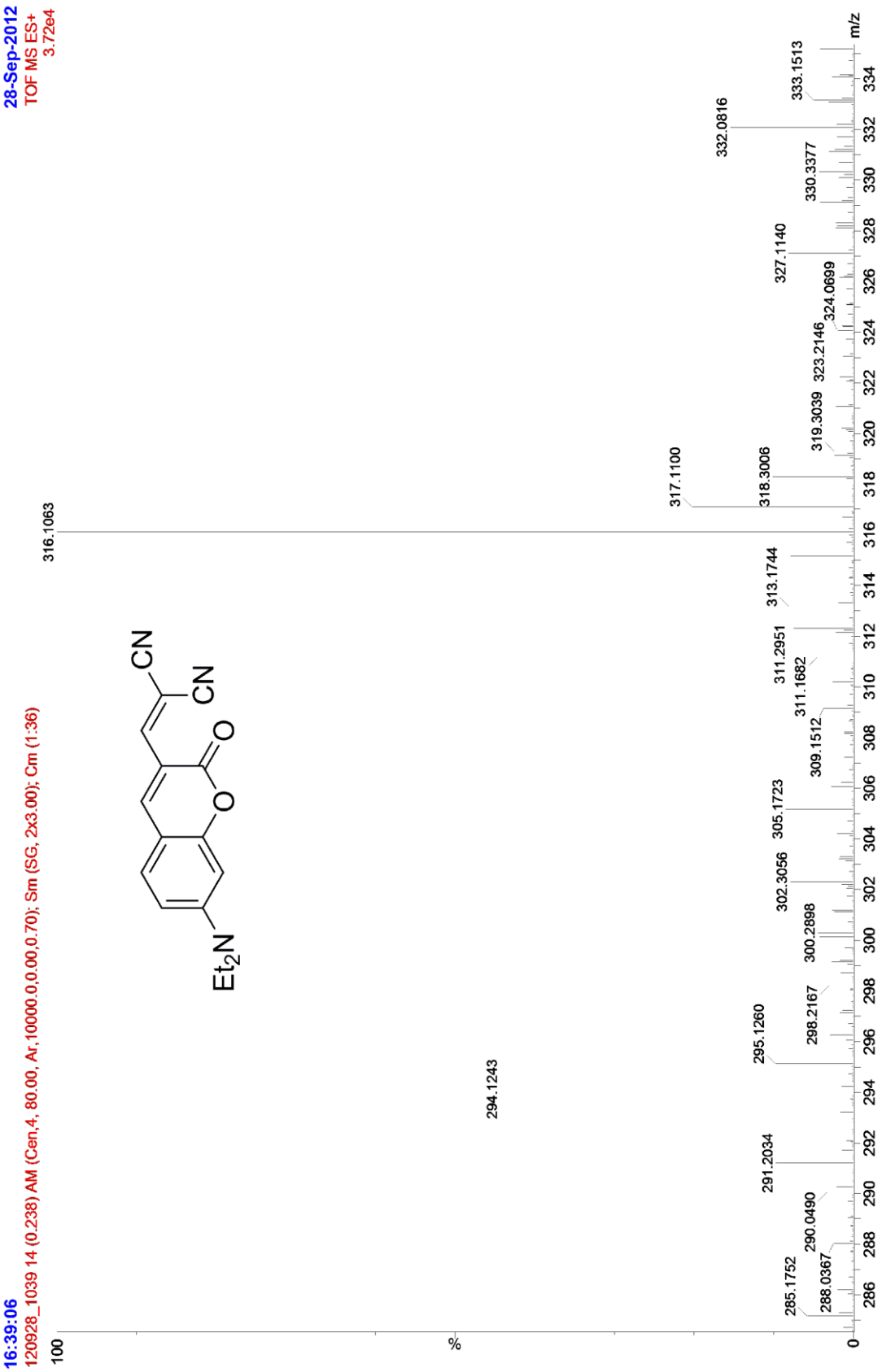
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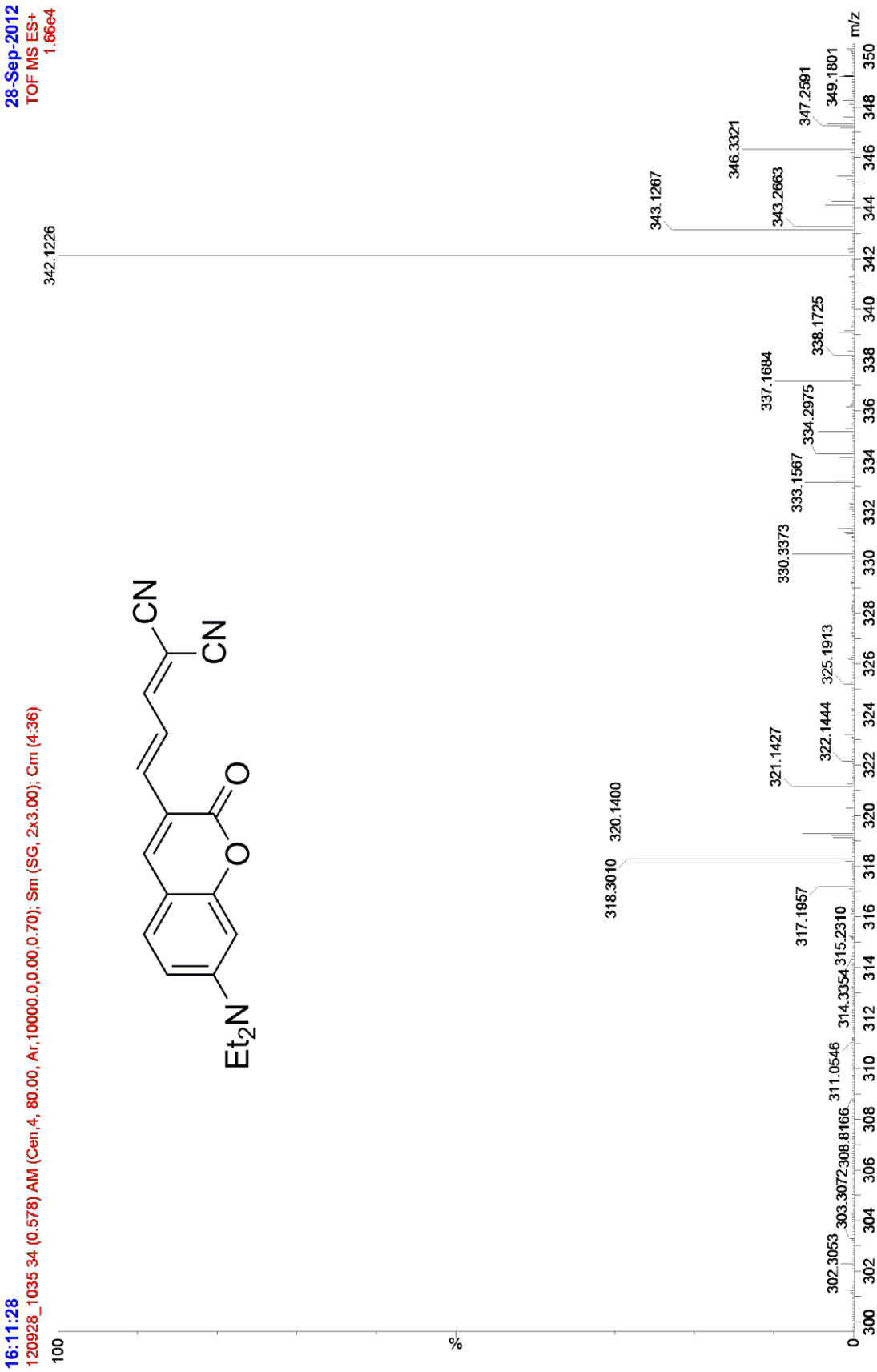
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18-Oct-2012
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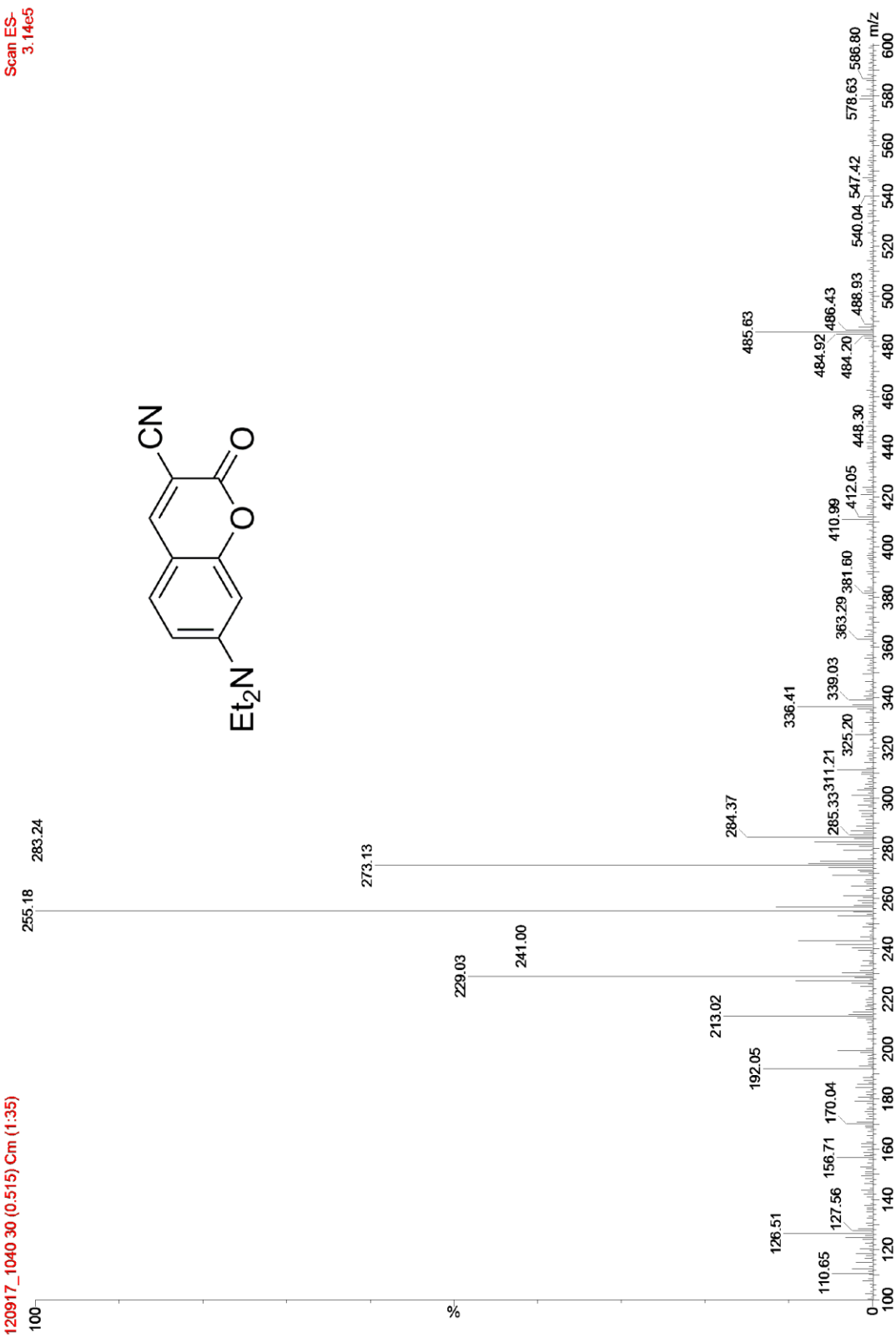
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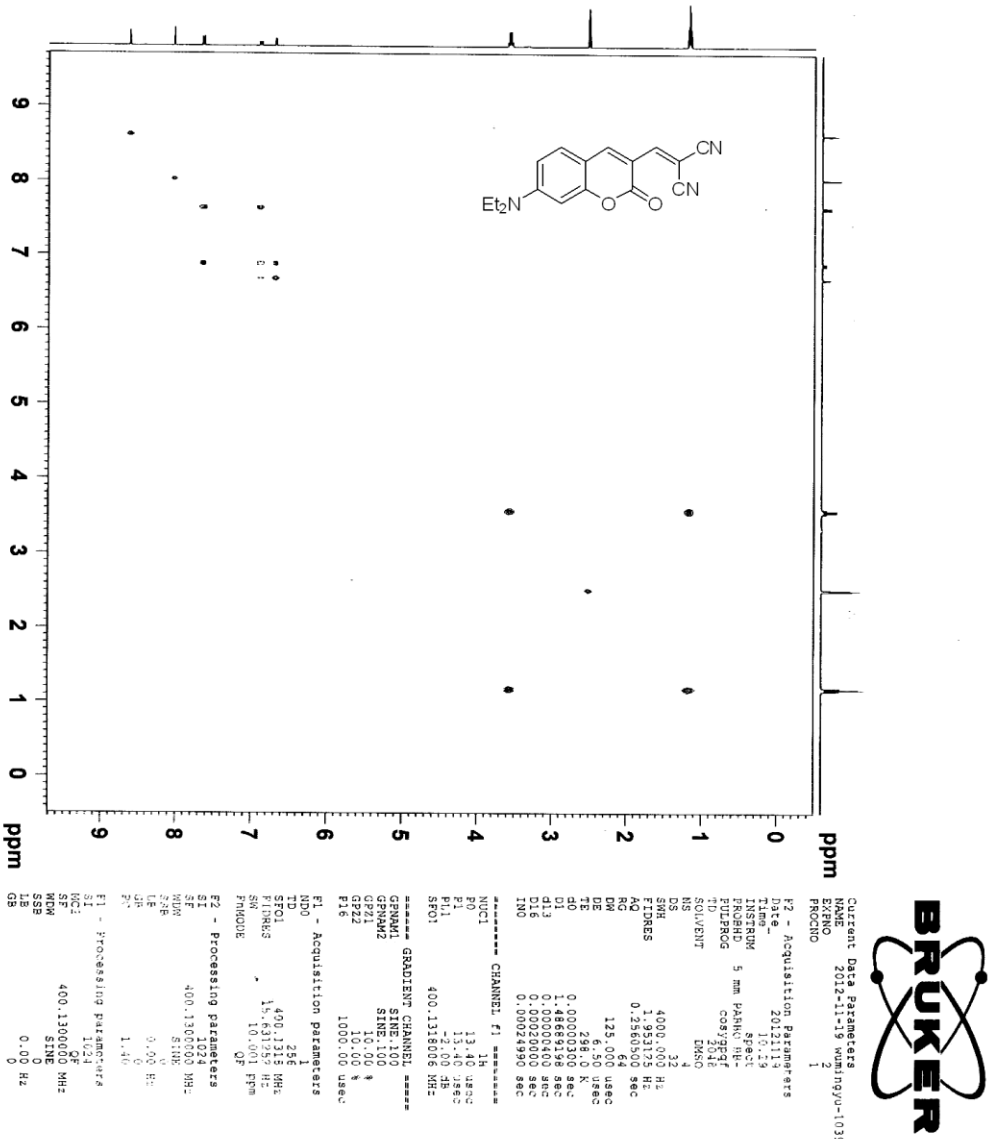
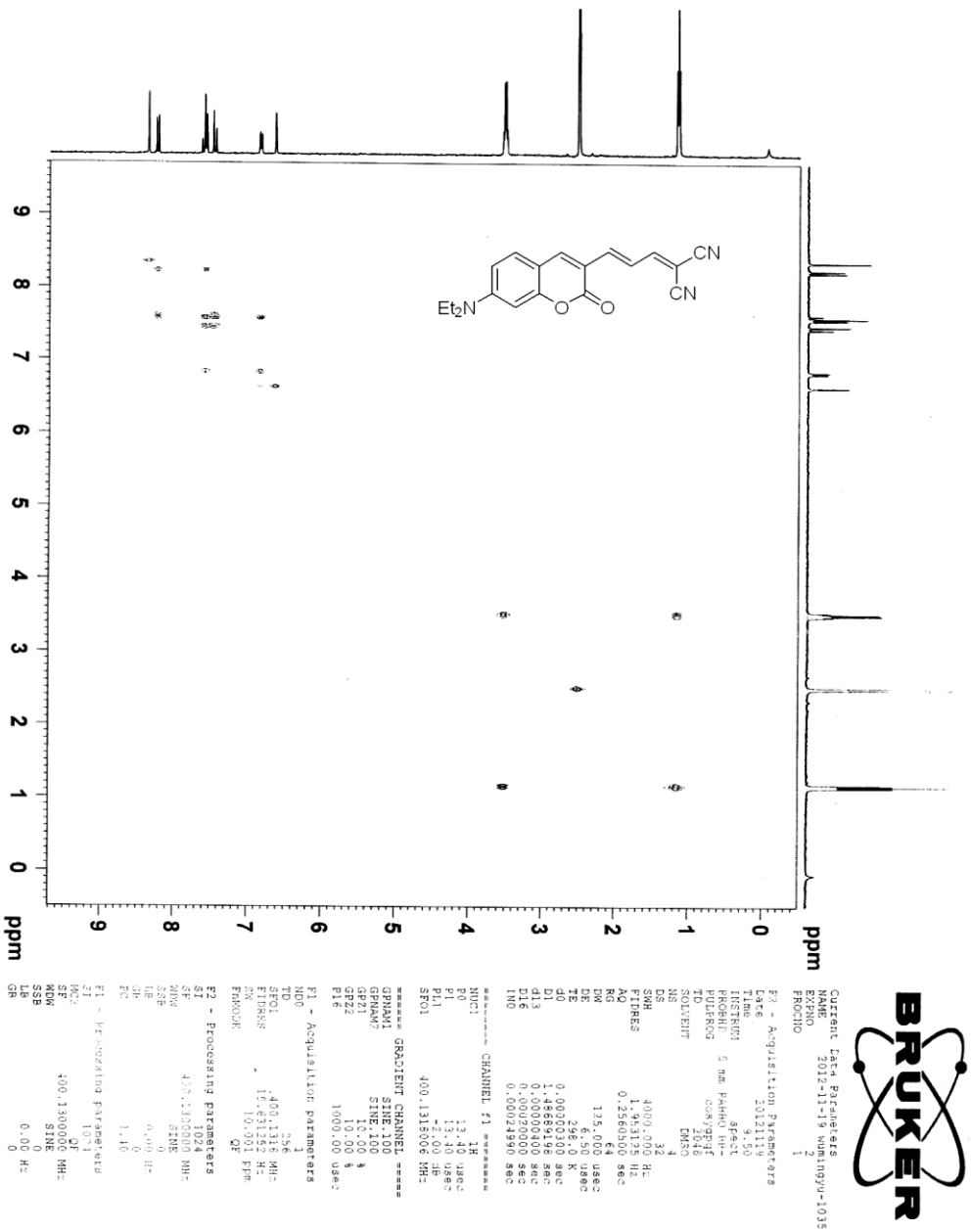
^{1}H-^{1}H COSY spectrums of probe 1 and probe 2

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