Supporting Information

A Green Chemical Approach for the *N*-alkylation of Aldoximes to form Nitrones in Organized Aqueous Media and Their *In Situ* Cycloaddition with Olefins

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I. General procedure for the preparation of oxime: 1 gm of hydroxylamine hydrochloride and 2 gm of crystalline sodium acetate were dissolved in 8-10 ml of water. Then one aromatic or aliphatic aldehyde was added to it and shaken. Sonication may also be performed for better result. If the reaction mixture turned turbid or the aldehyde became immiscible with water, then rectified spirit was added dropwise with shaking until a homogeneous layer appeared. Then the reaction mixture was warmed on water bath for 8-10 minutes and then poured into 50 ml of ice-cold water with constant sirring with a glass rod. The oxime separated out. The solid was filtered and washed with cold water and lastly with cold petroleum ether. It was then recrystallised from alcohol-water.

II. General procedure for the preparation of maleimide: The apparatus consists of a 500 ml two-necked round bottom flask equipped with a reflux condenser and a 50 ml dropping funnel. 10 gm (102 mmols) of maleic anhydride and 150 ml of dry diethyl ether are taken in the flask. Slow stirring is started and, when all the maleic anhydride has dissolved, a solution of 10 ml (10.2 gm, 110 mmols) of aniline in 15 ml of dry diethyl ether is added through the dropping funnel. The addition must be fast enough and the stirring rate is increased. A thick suspension appeared and it is stirred at room temperature for 1.5 hr and is then cooled in an ice bath. The product is filtered under suction. In another 250 ml r. b. flask 40 ml of acetic anhydride and 3.7 gm of anhydrous sodium acetate are added with stirring. Then the filtered product, obtained as described above, is added to it and the resulting suspension is dissolved by constant stirring on a steam bath for 20-30 mins. The reaction mixture is then poured into 100 ml of ice-water. The product obtained is filtered under suction and washed thoroughly with 25 ml of ice-cold water for three times and once with 25 ml of ice-cold petroleum ether. The product is obtained in good yield and it was recrystallised from cyclohexane giving bright yellow needle shaped crystalline compound (mp. 90^0C).

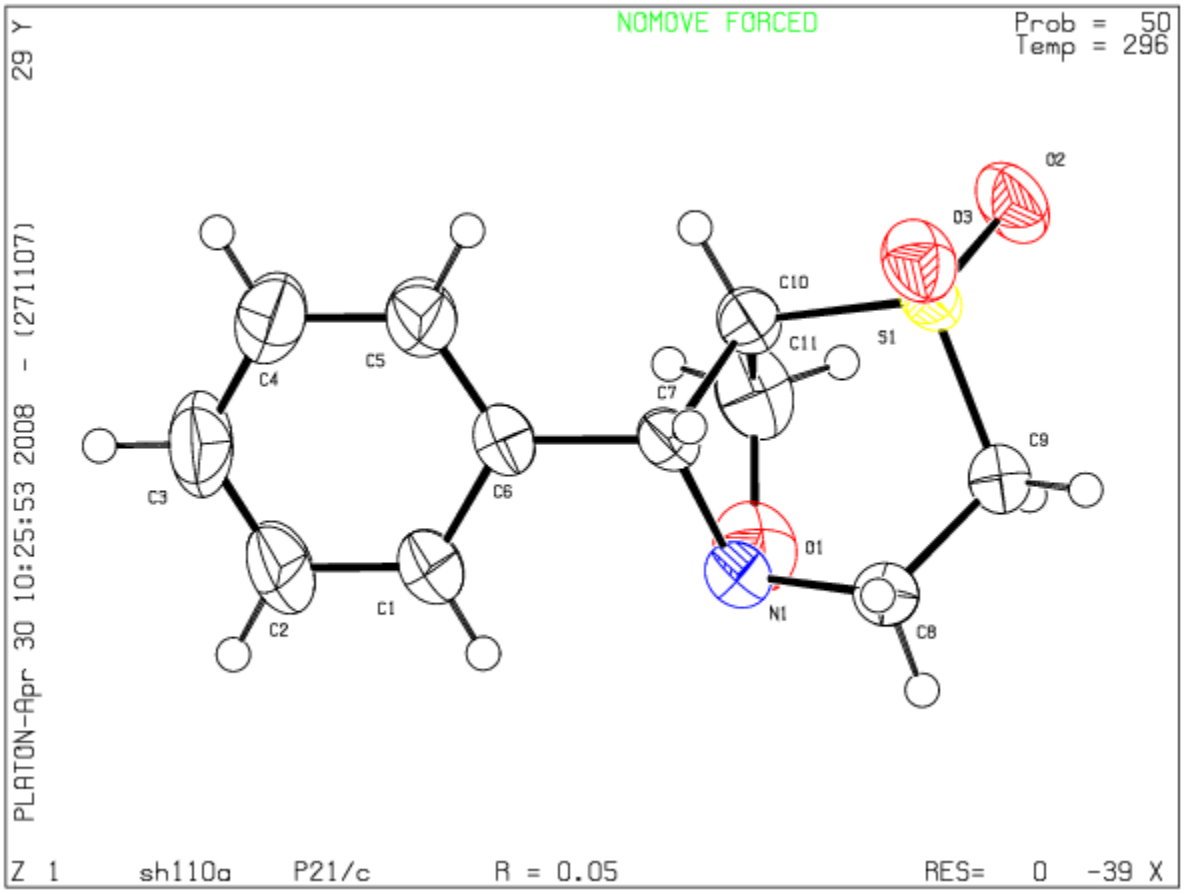
III. X-ray crystallographic data of 6a:

Crystal data of compound 6a: $C_{11}H_{13}NO_3S$, FW = 239.28, monoclinic, space group P21/c, a = 17.1392 (5) Å, b = 6.0512 (2) Å, c = 10.9857 (4) Å, β = 93.007 (2)^0, V = 1137.79 (7) Å^3, Z = 4, T = 296 (2) K, d_{calcd} = 1.397 g cm^{-3}, F (000) = 504. Diffraction data were measured with Mo K_α (λ = 0.71073 Å) radiation at 296 K using a Bruker Kappa Apex 2 system. A total of 2660 unique reflections were measured (θ_{max} = 30.87^0). Data analyses were carried out with the Difference Vectors program. The structures were solved by direct methods using the SHELXS-97[1] program. Refinements were carried out with a full matrix least squares method against F^2 using SHELXL-97.[2] Non-hydrogen atoms were refined with anisotropic thermal parameters. The final R value was R1 = 0.0456 and wR2 = 0.1500 with $I > 2\sigma(I)$. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with reference numbers CCDC 686184.

Ref.

(1) Sheldrick, G. M. *Acta Crystallogr. A* **1990**, *46*, 467-473.

(2) Sheldrick, G. M. *SHELX97*: *Program for Crystallography Refinement*; University of Gottingen: Germany, 1997.



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IV. NMR spectrum of compound 4a-m and 6a-e:

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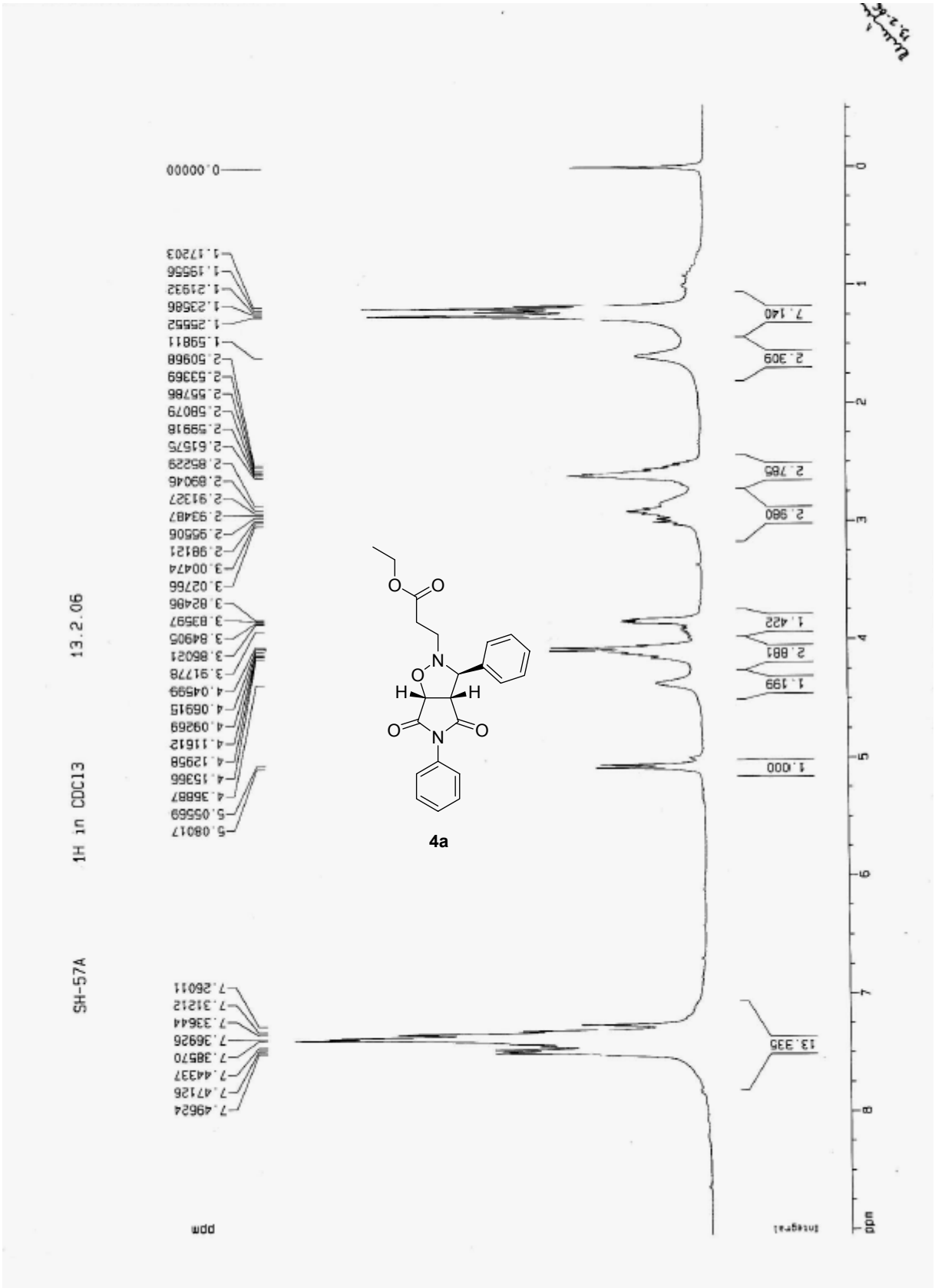

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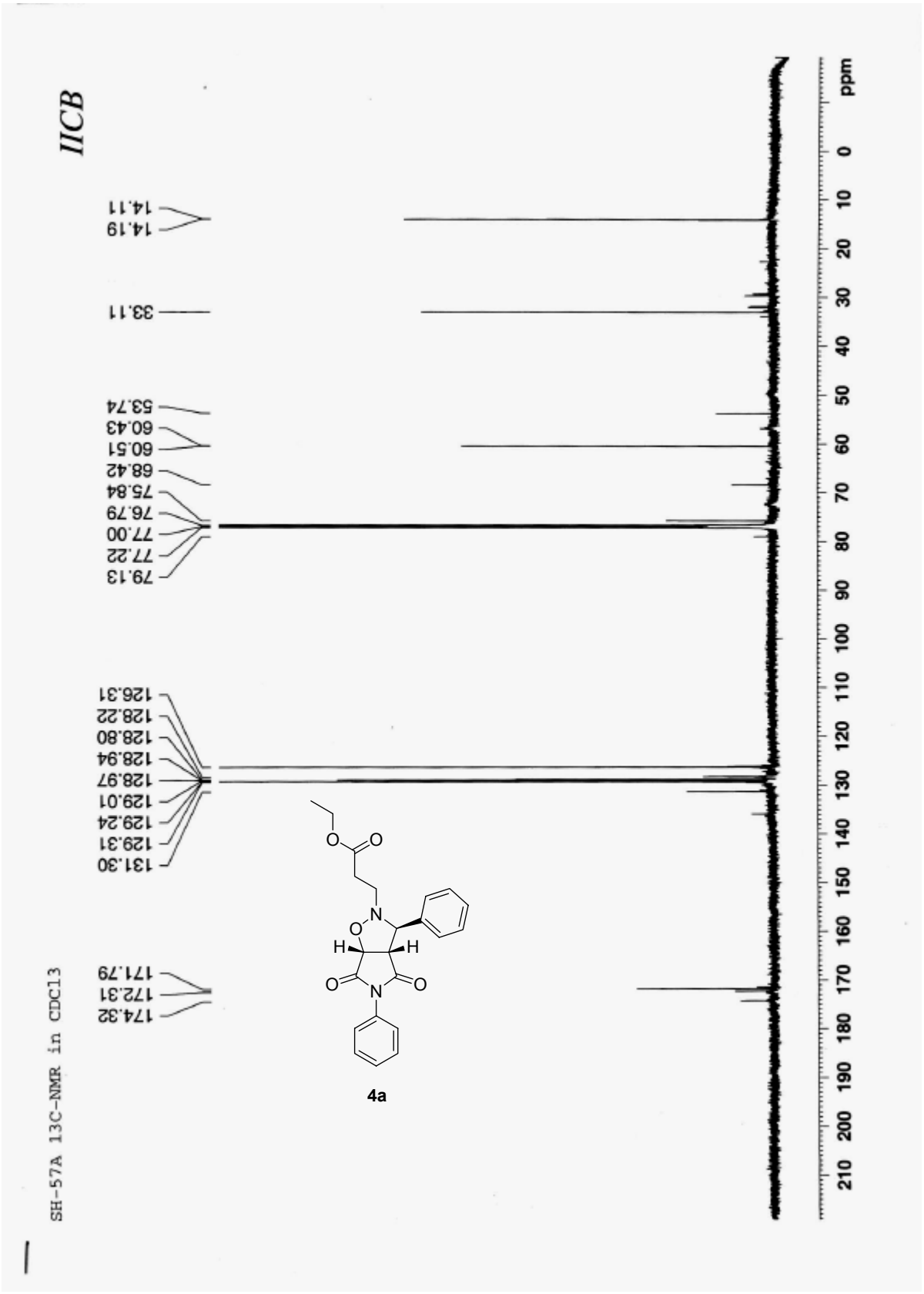

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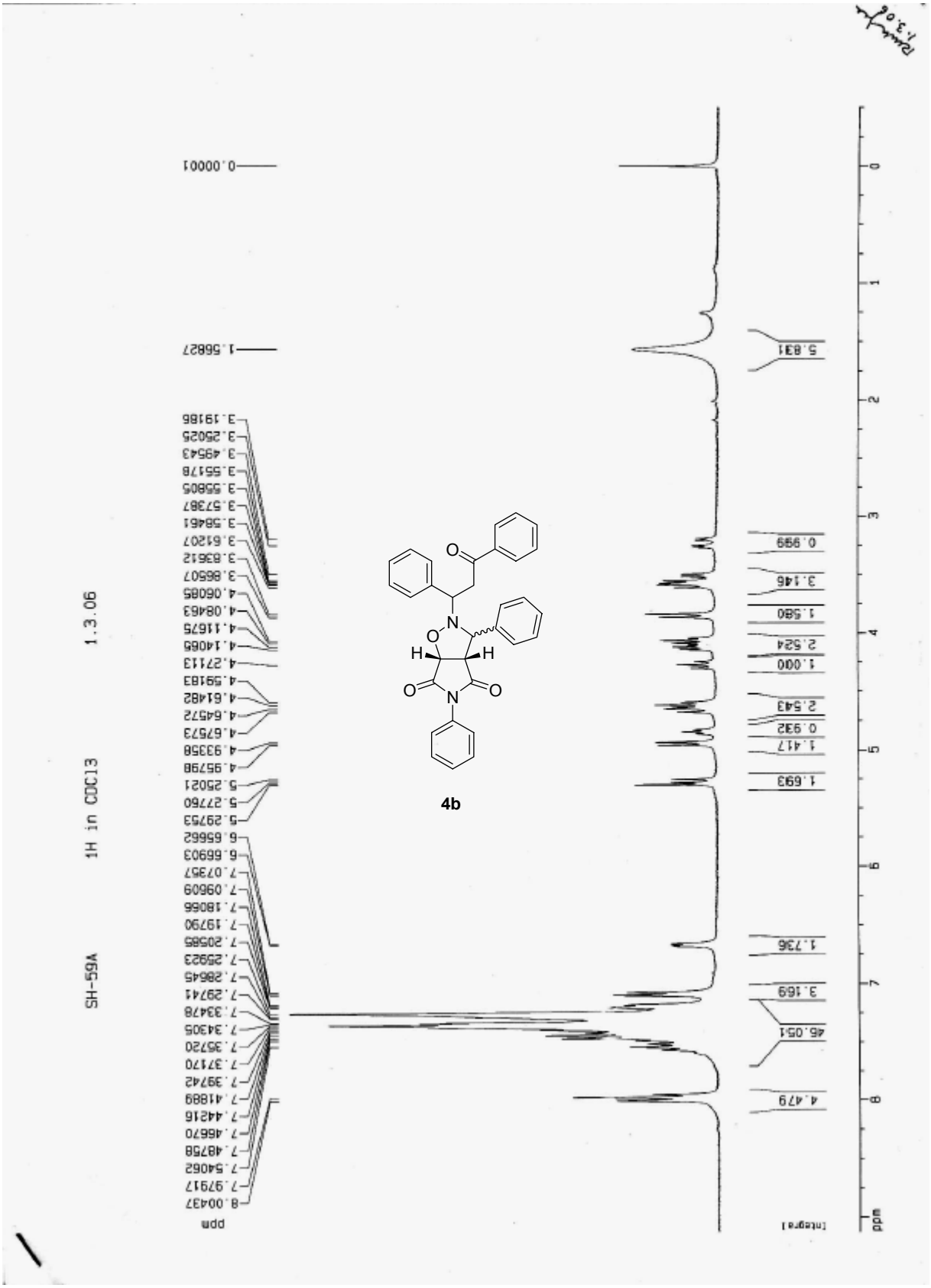

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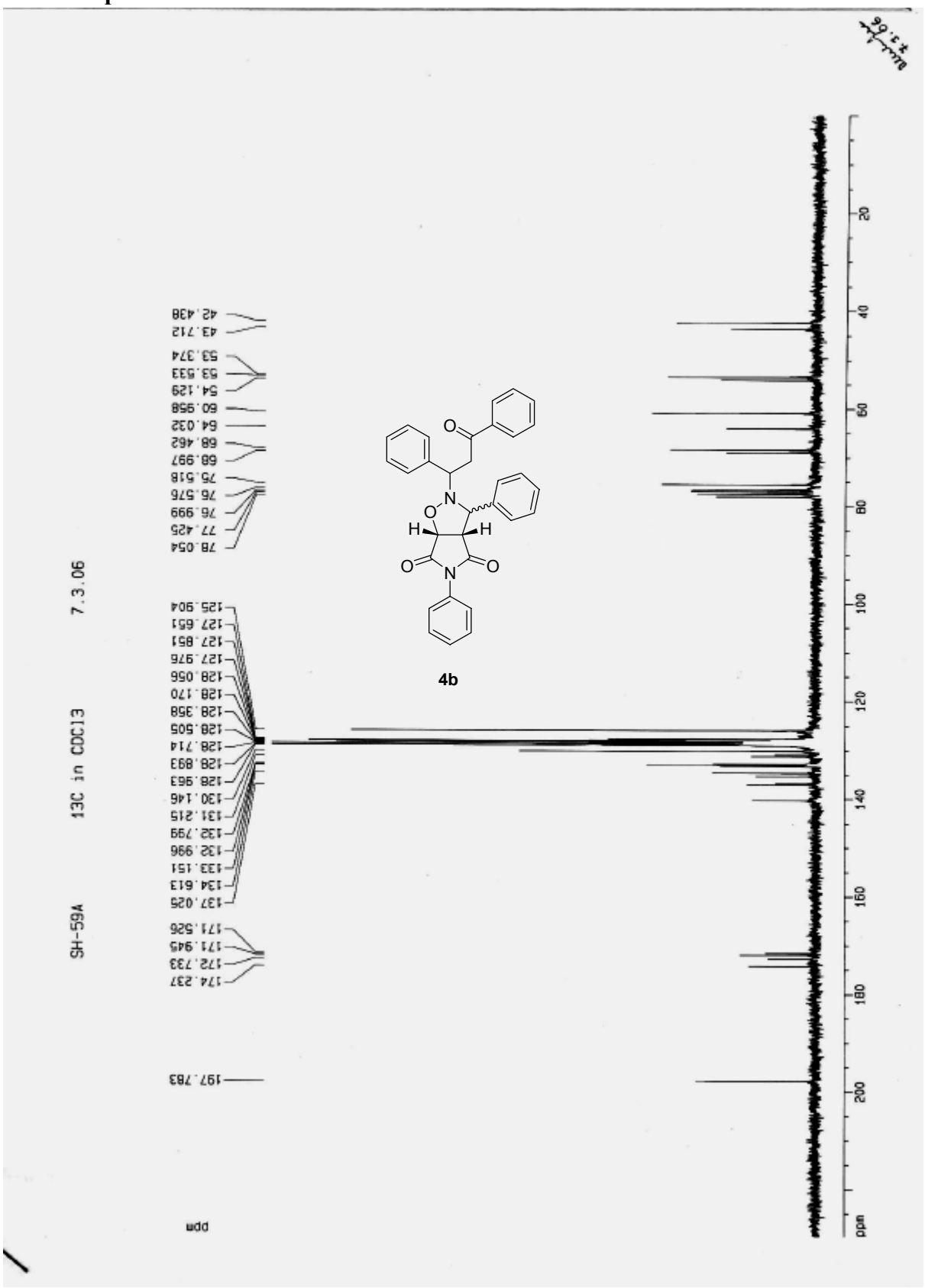

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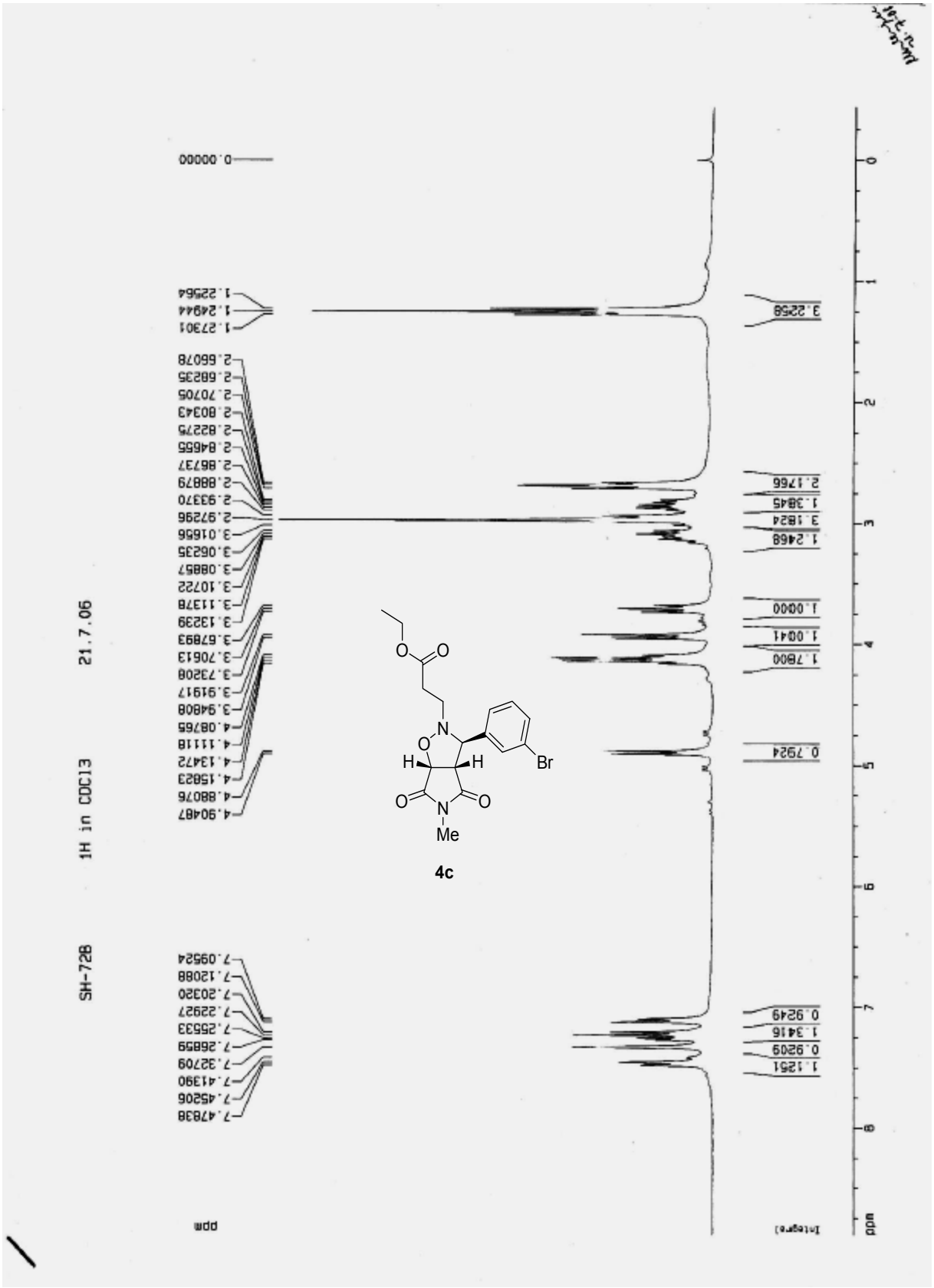

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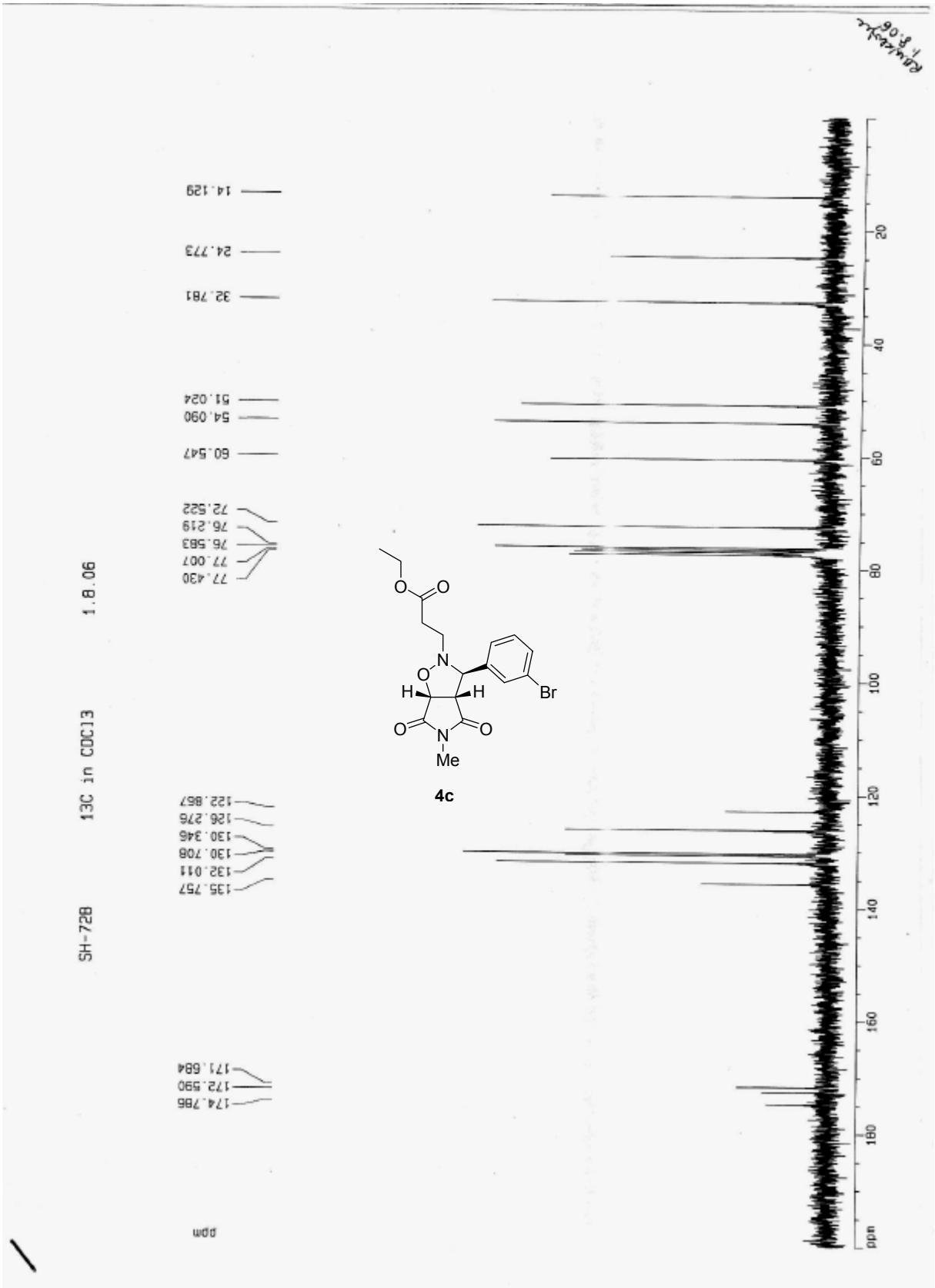

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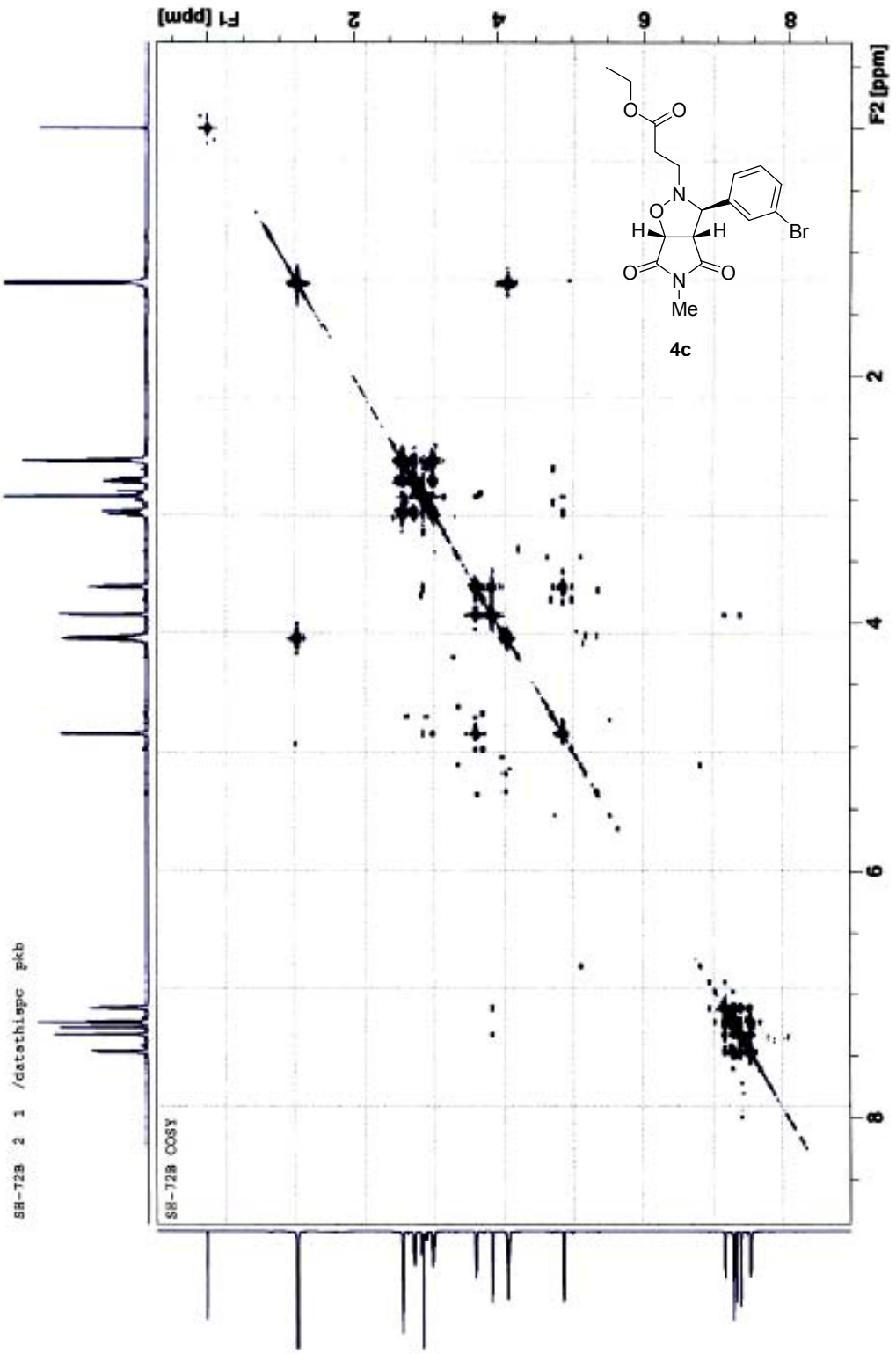

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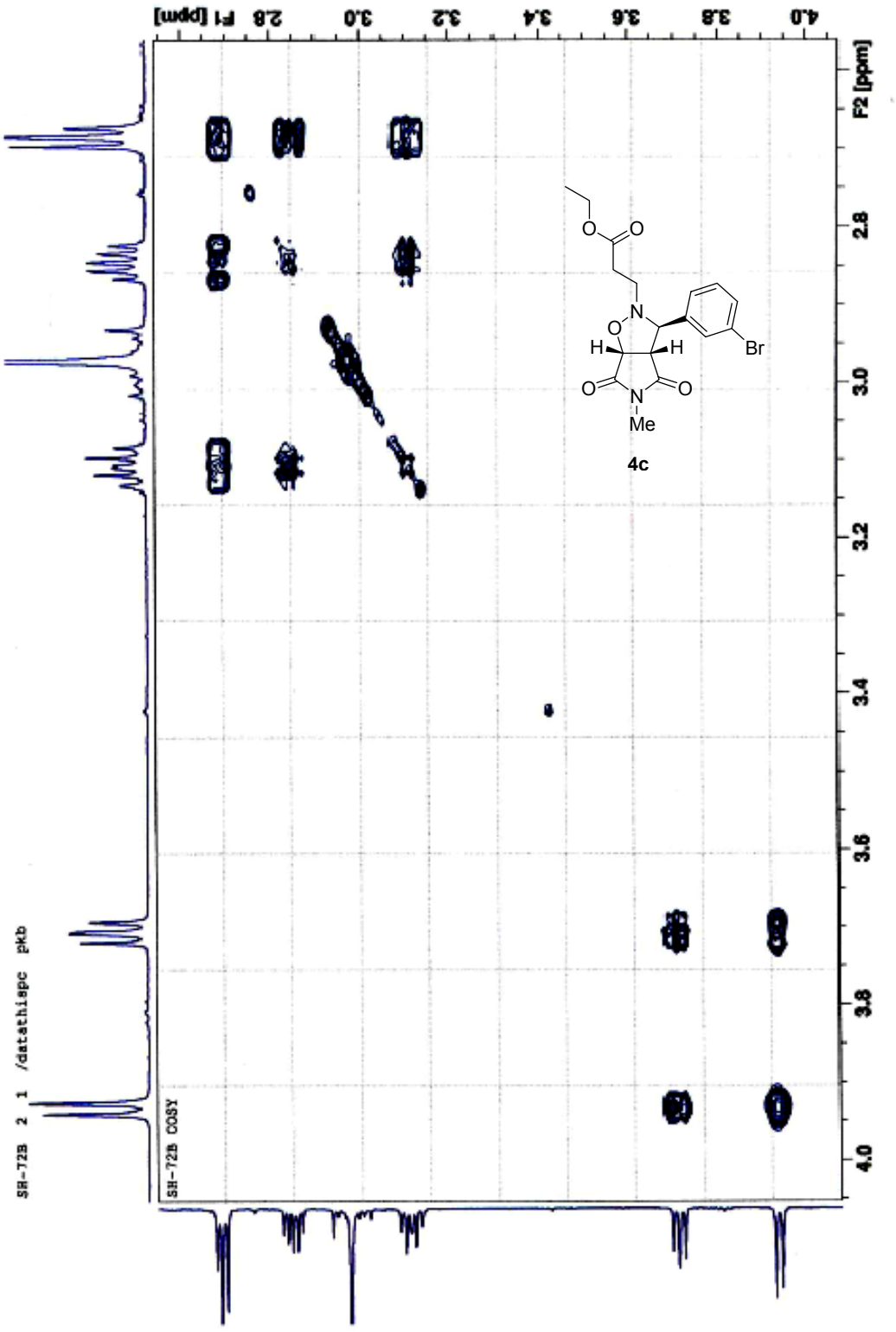

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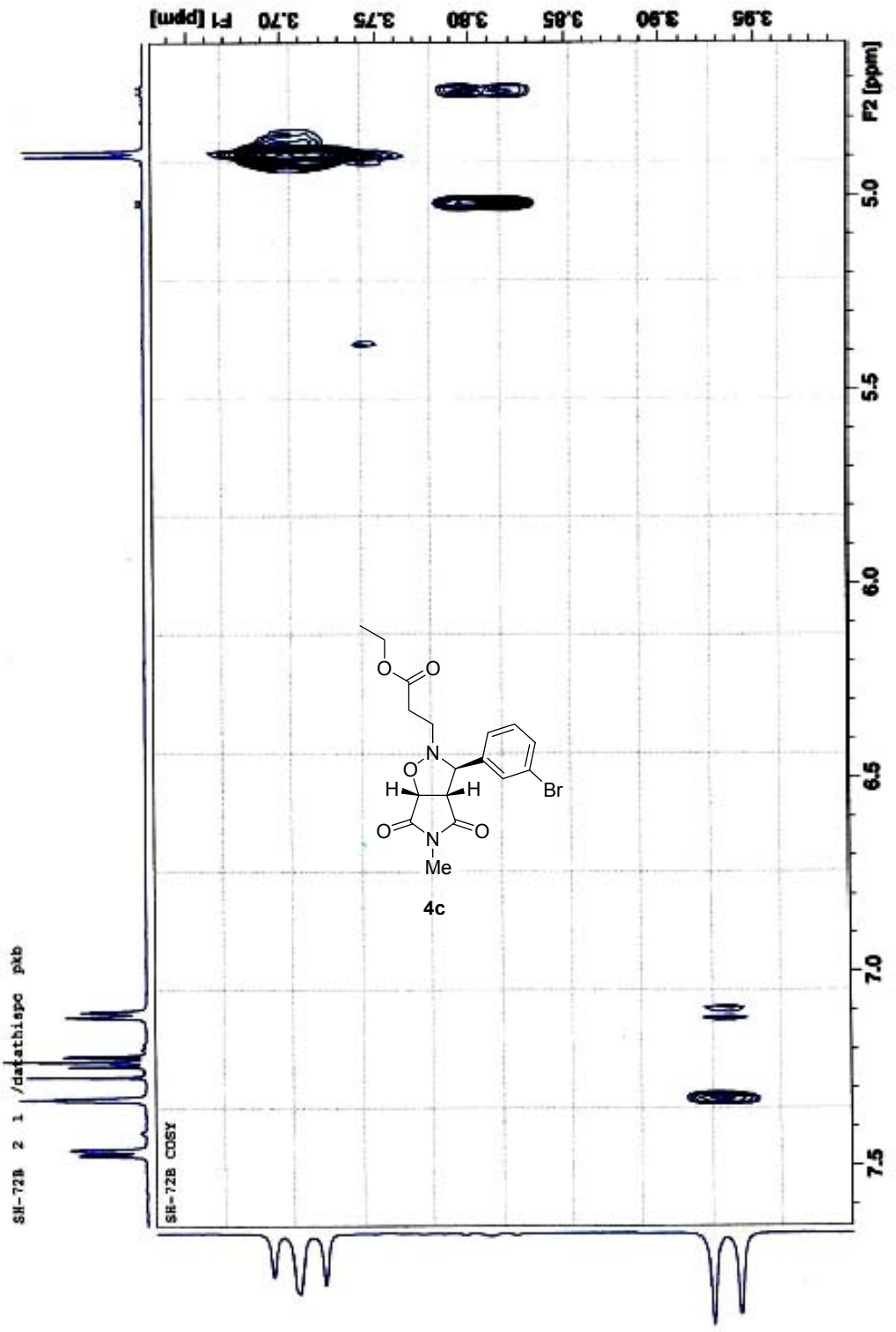

4c

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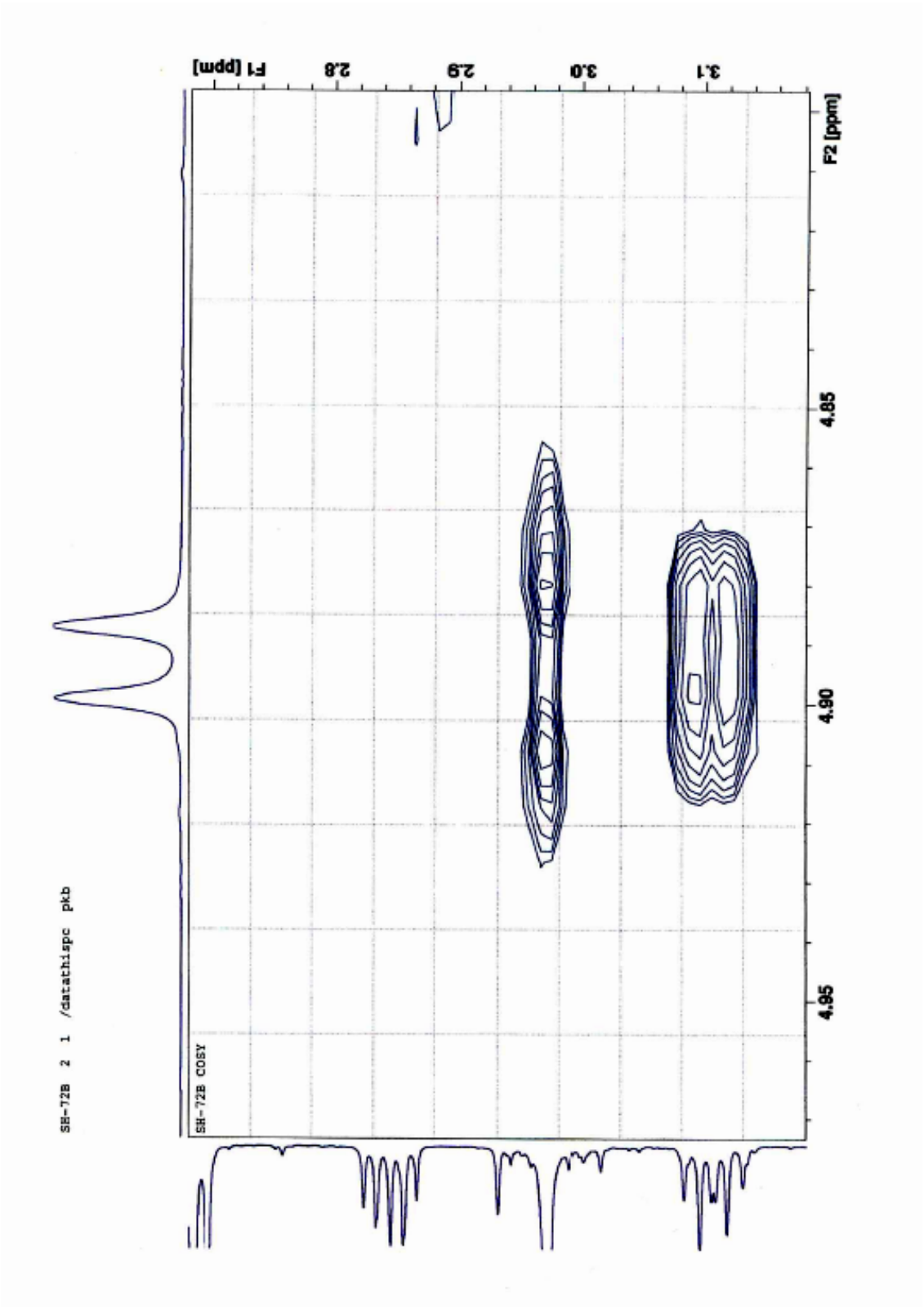

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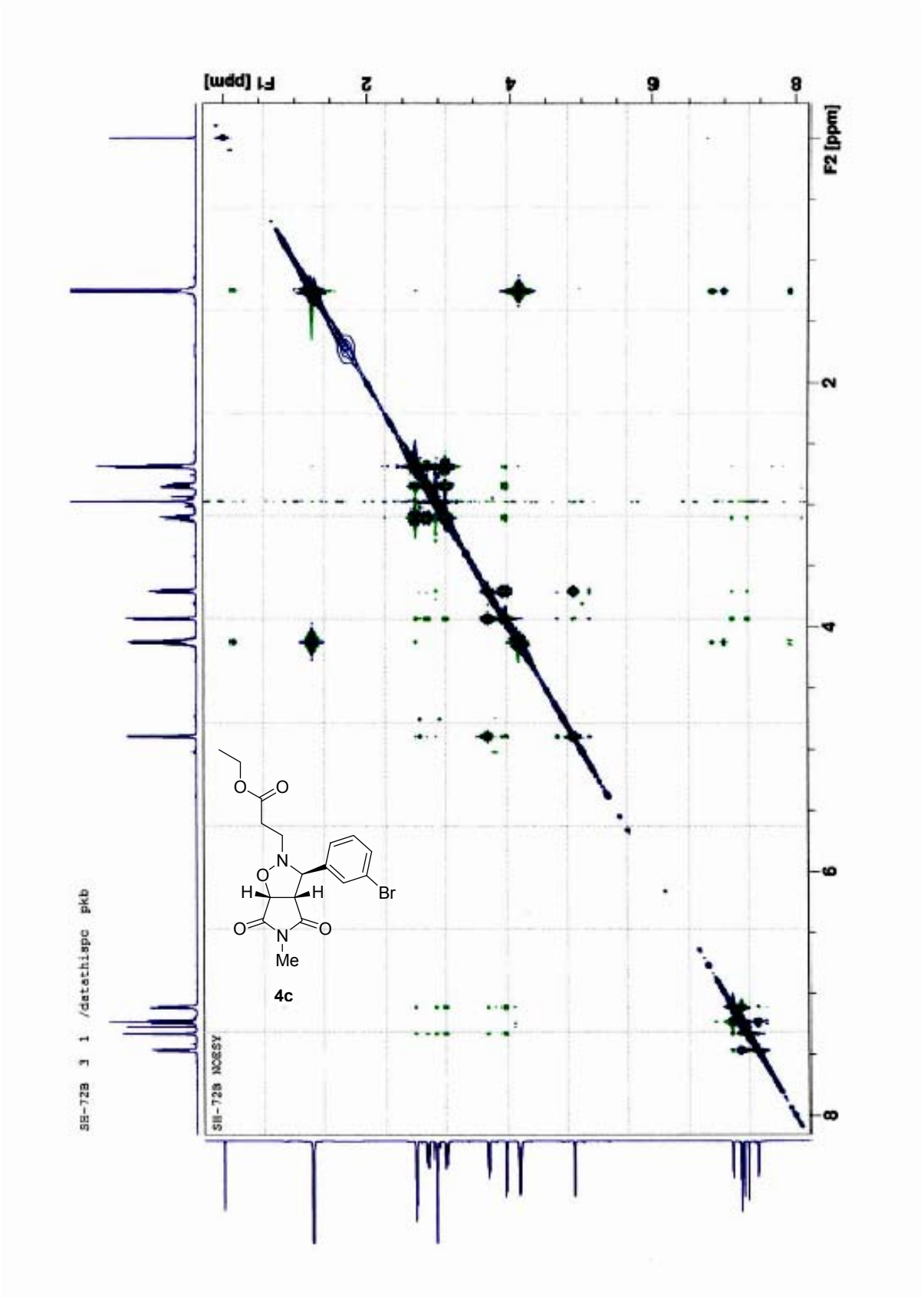

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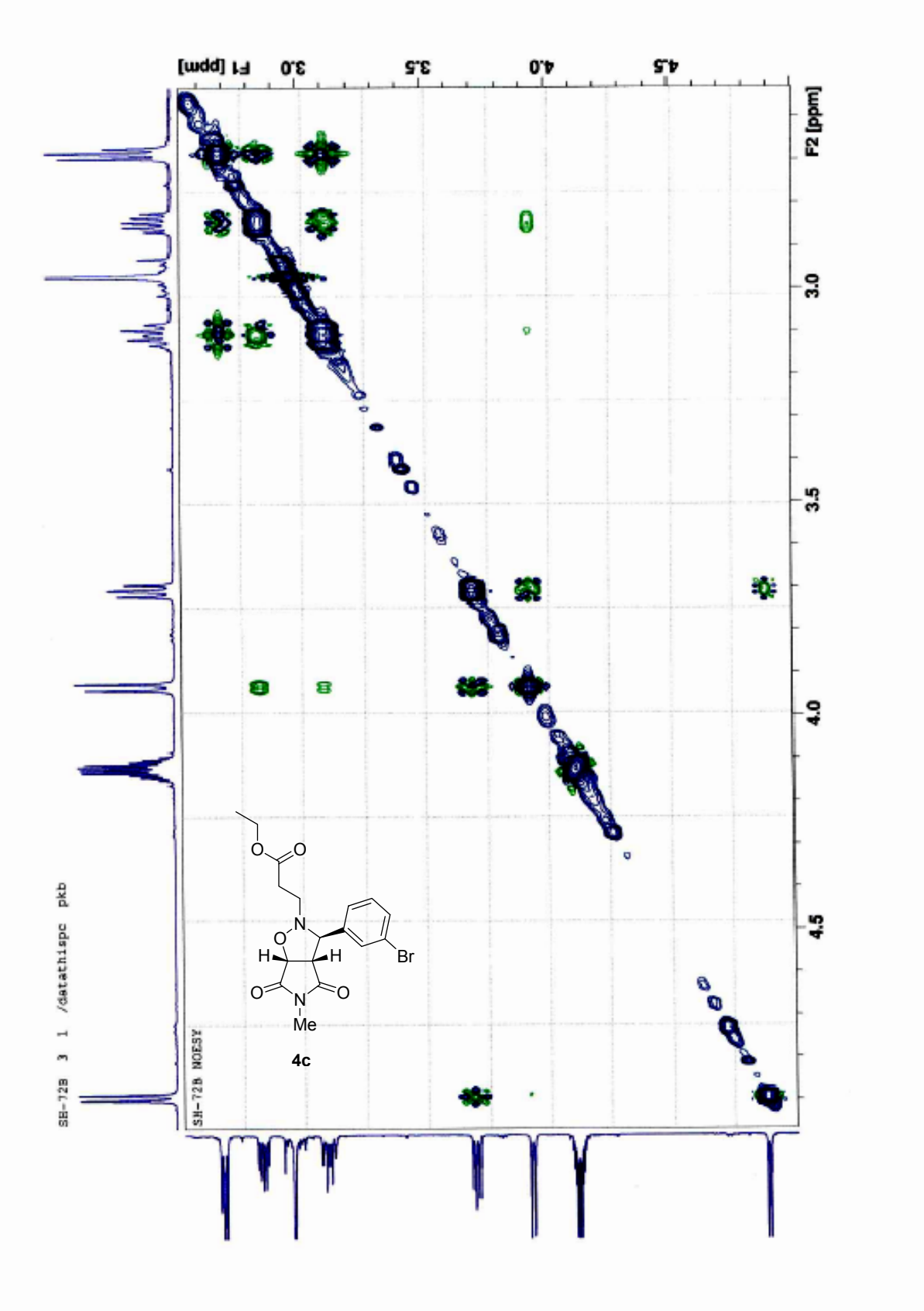
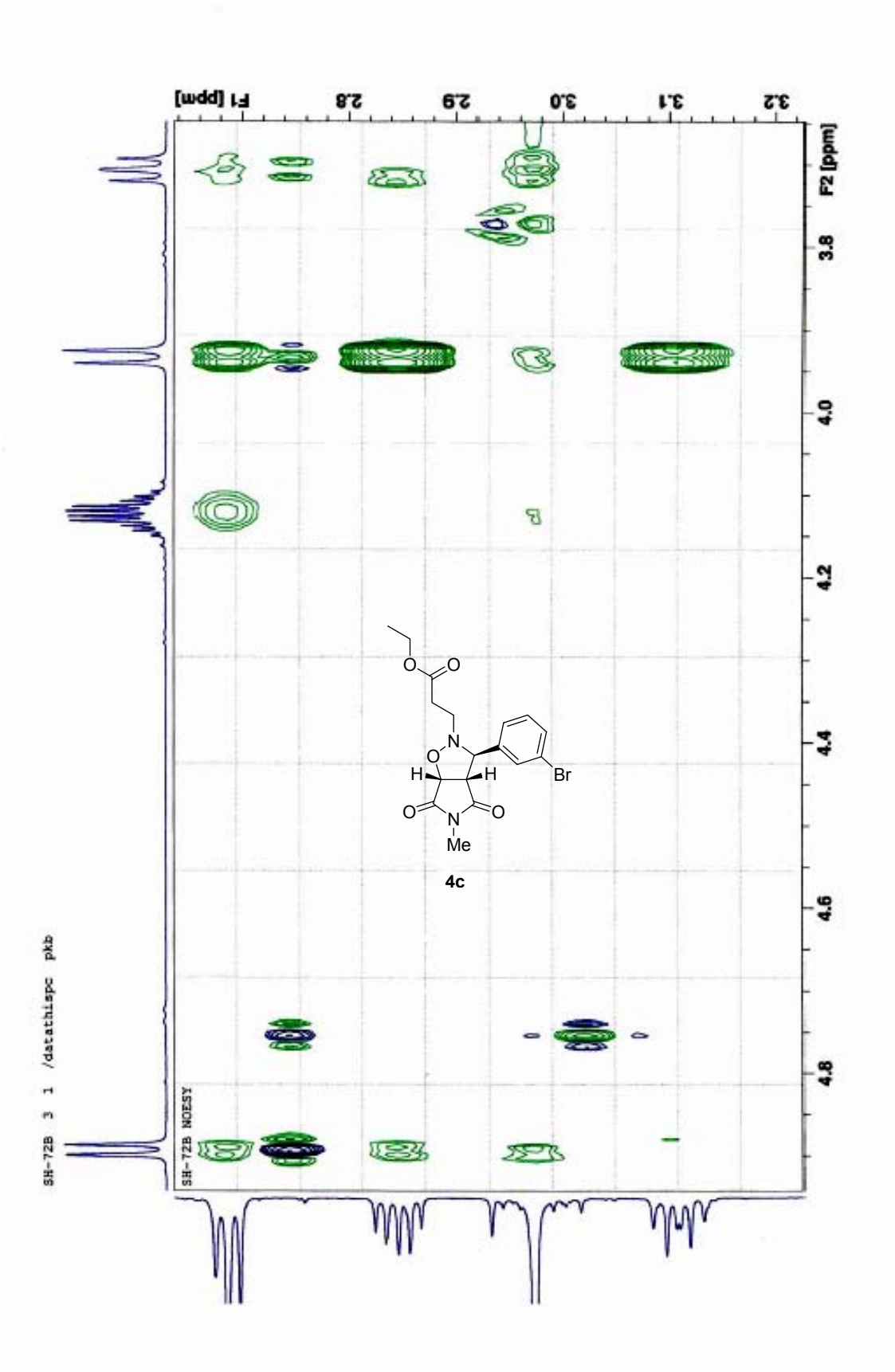


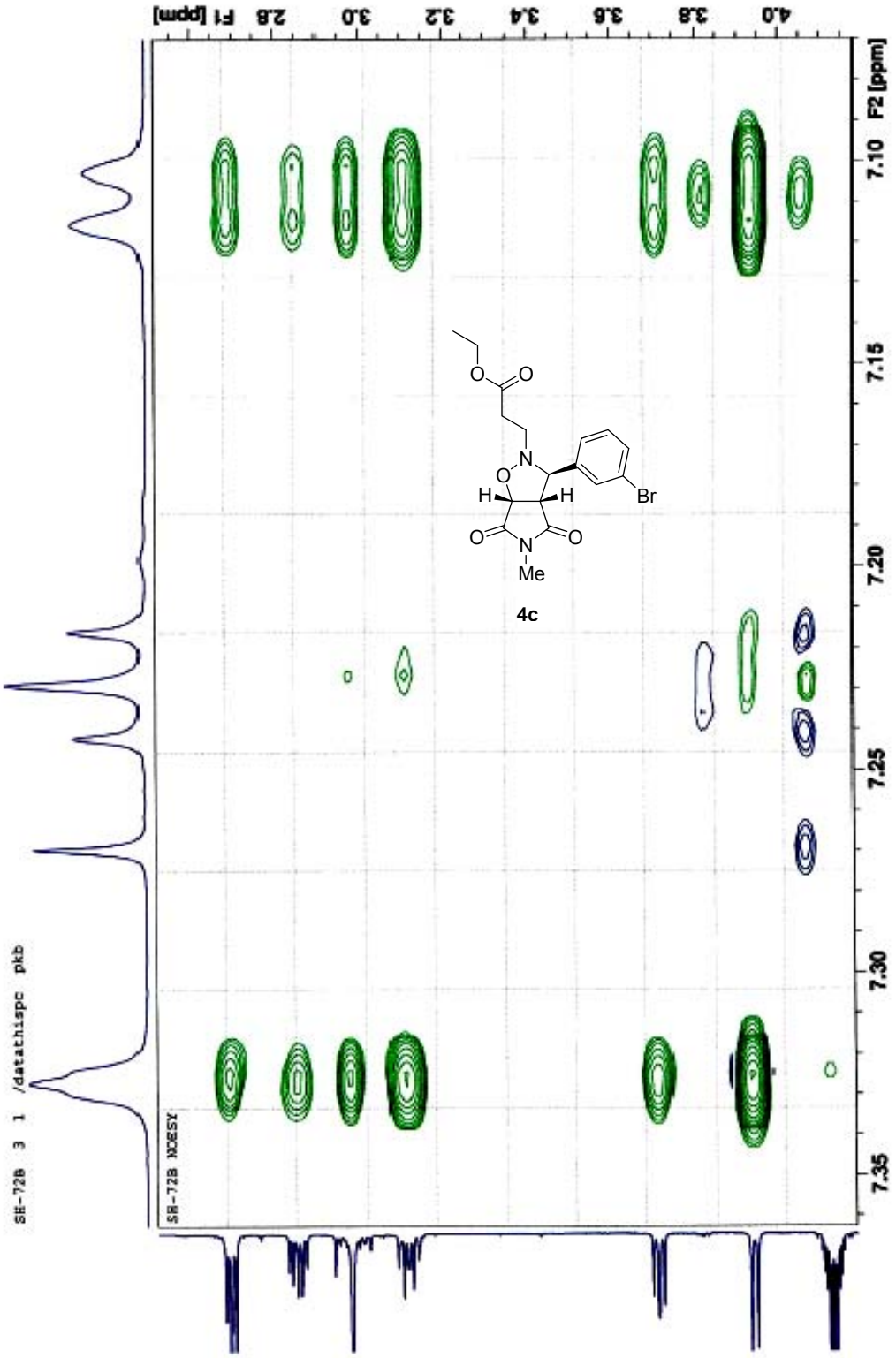
4c

Expansion (2) of NOESY Spectrum of 4c:

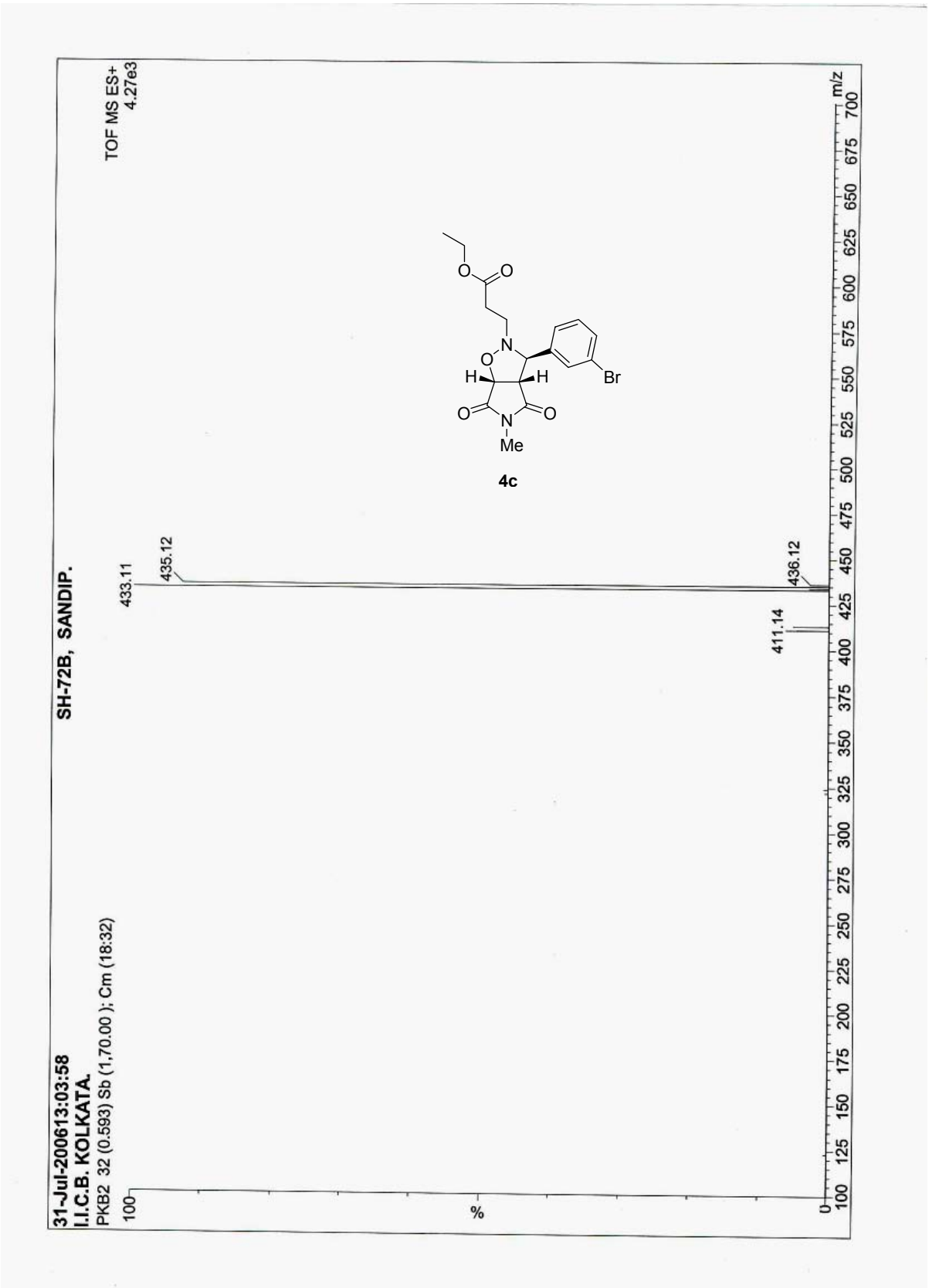


4c

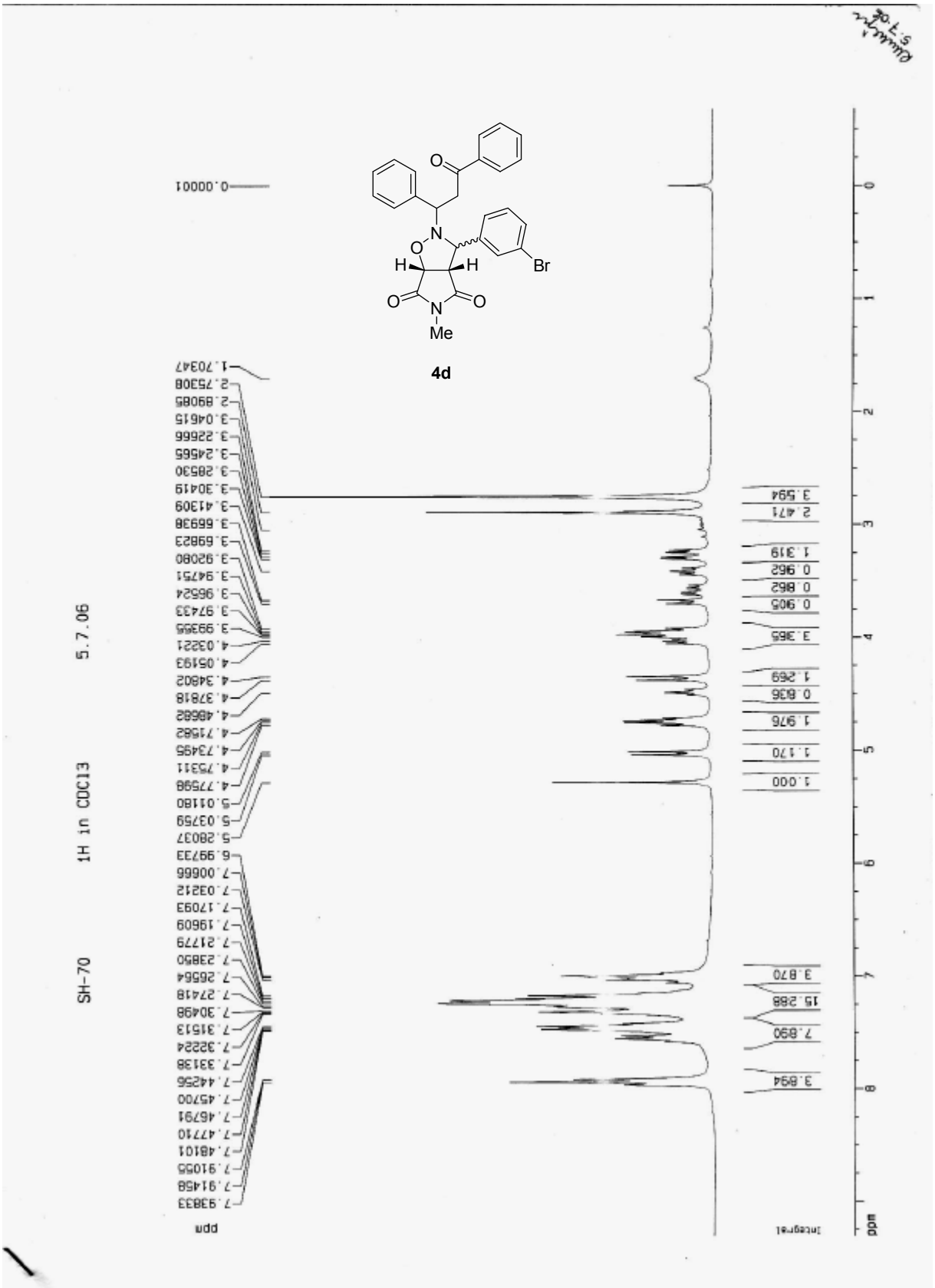
Expansion (3) of NOESY Spectrum of 4c:



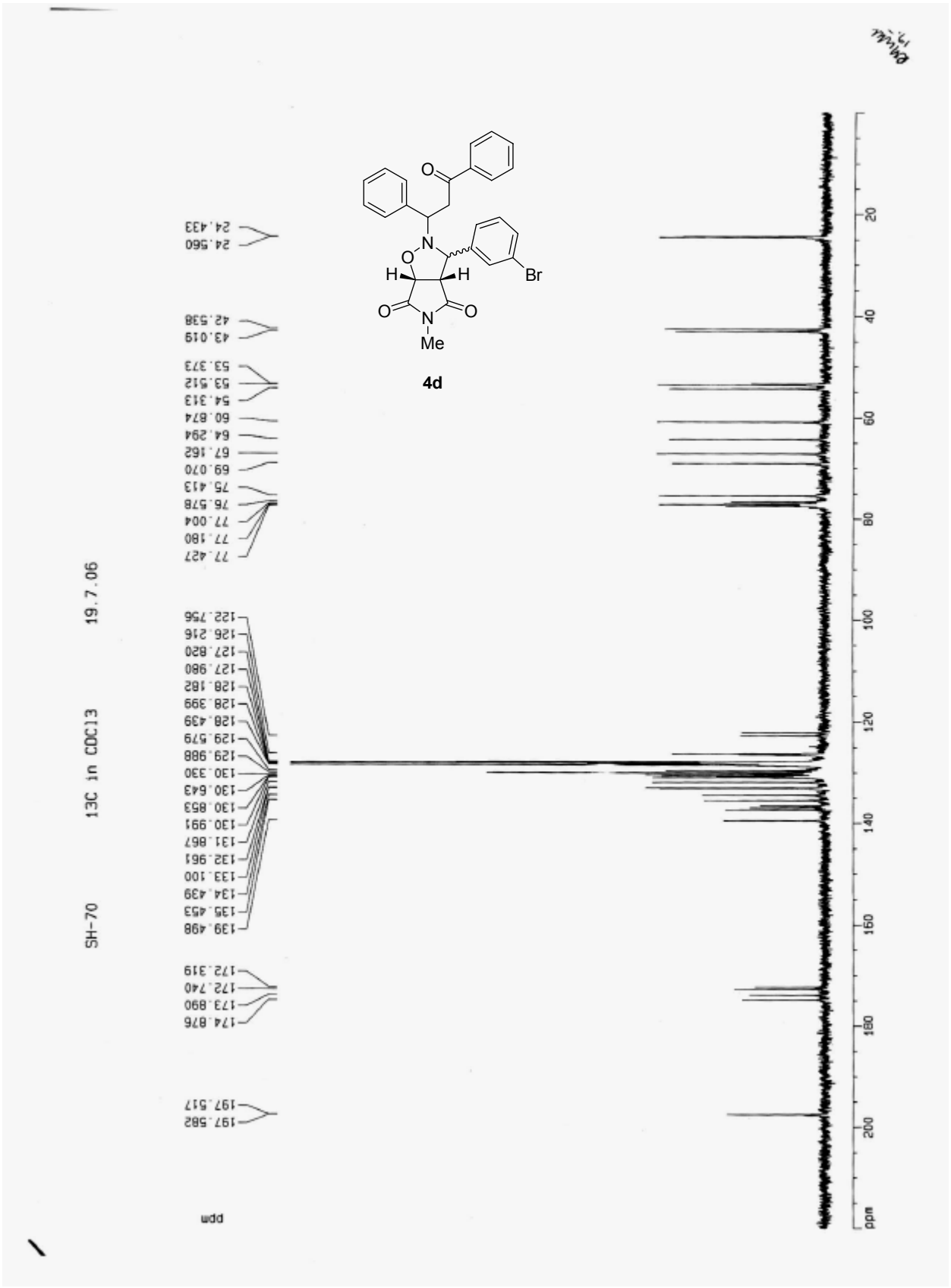
Mass Spectrum of 4c:



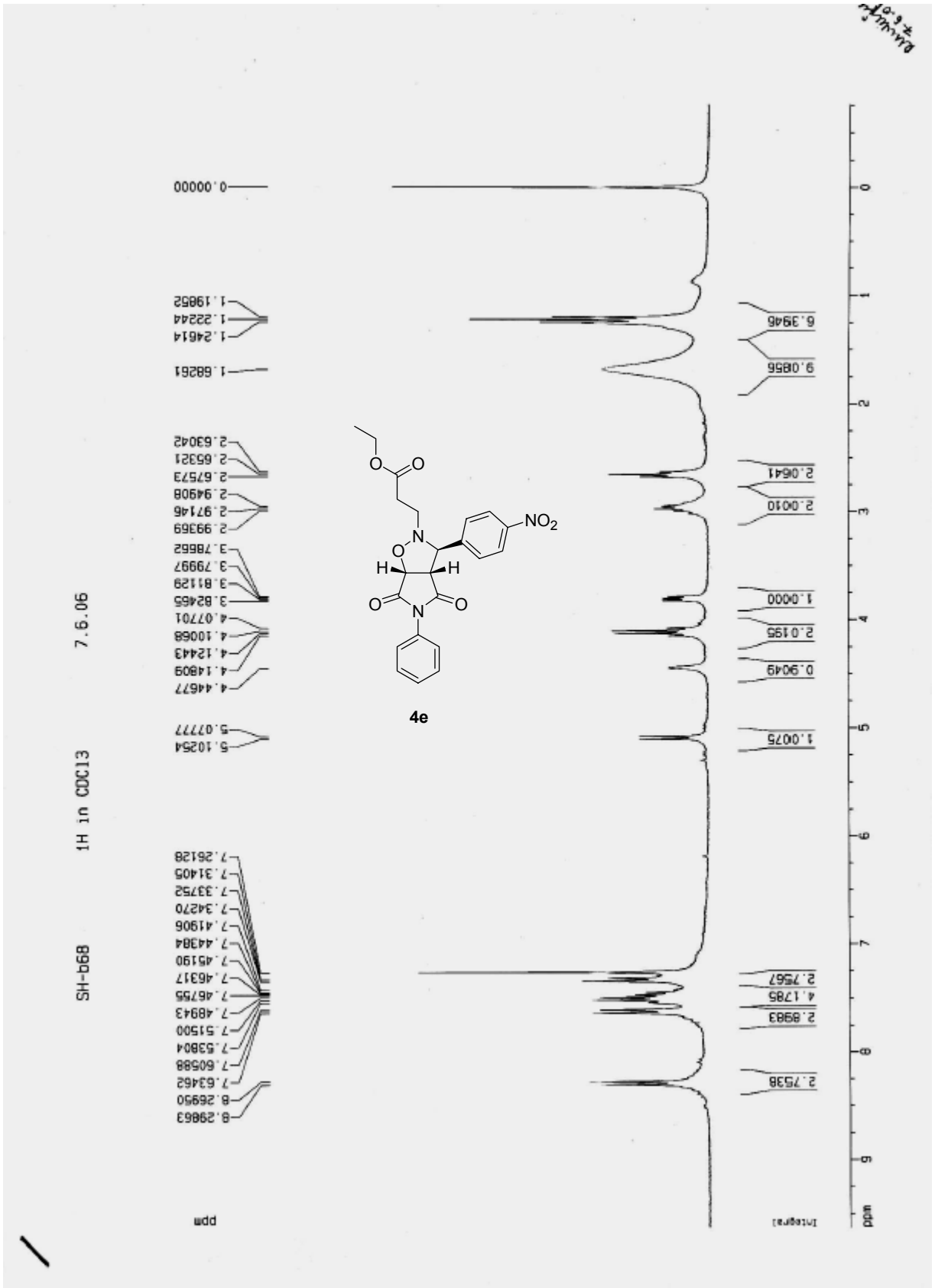
^{1}H NMR Spectrum of 4d:



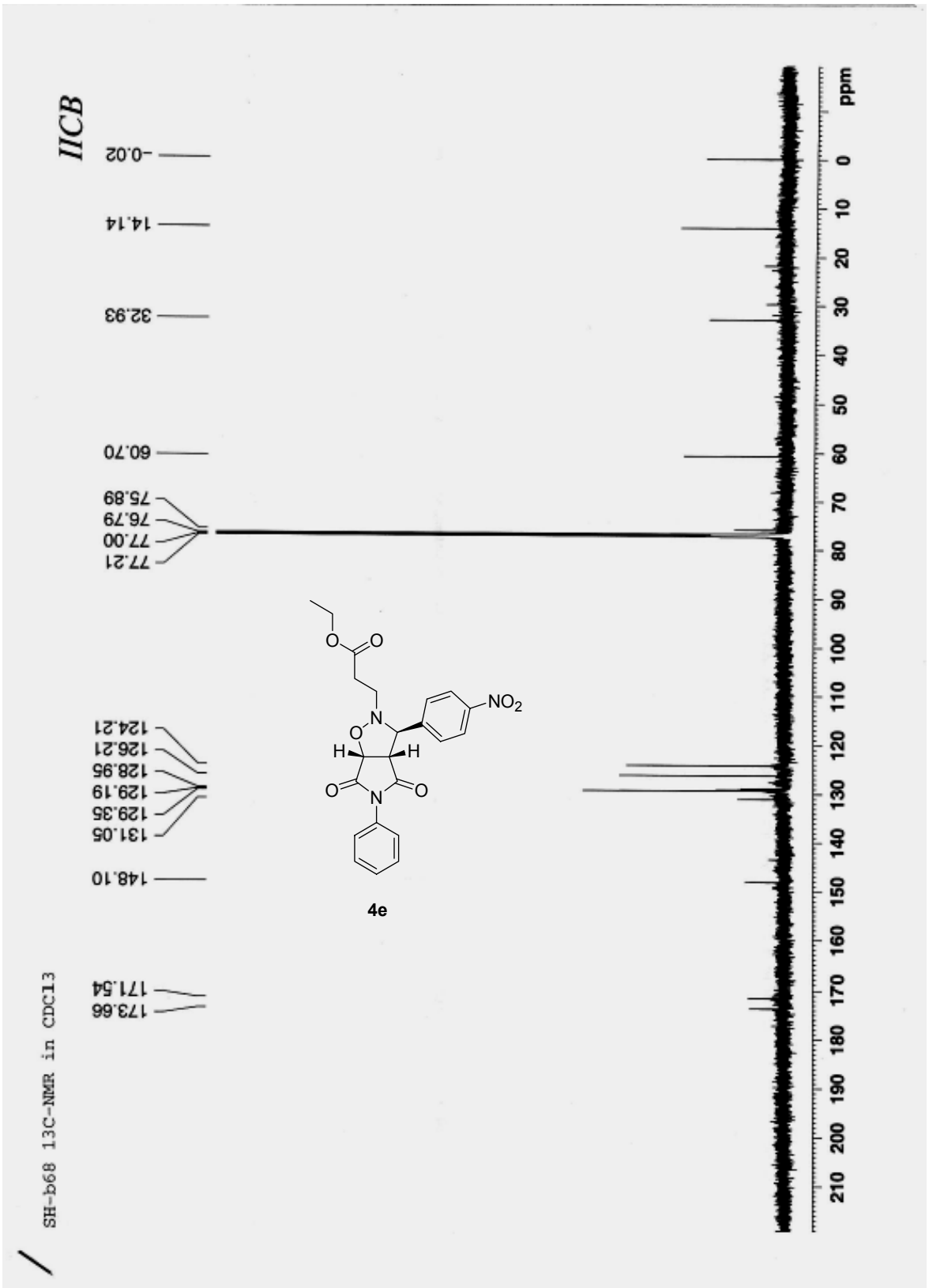
^{13}C NMR Spectrum of 4d:



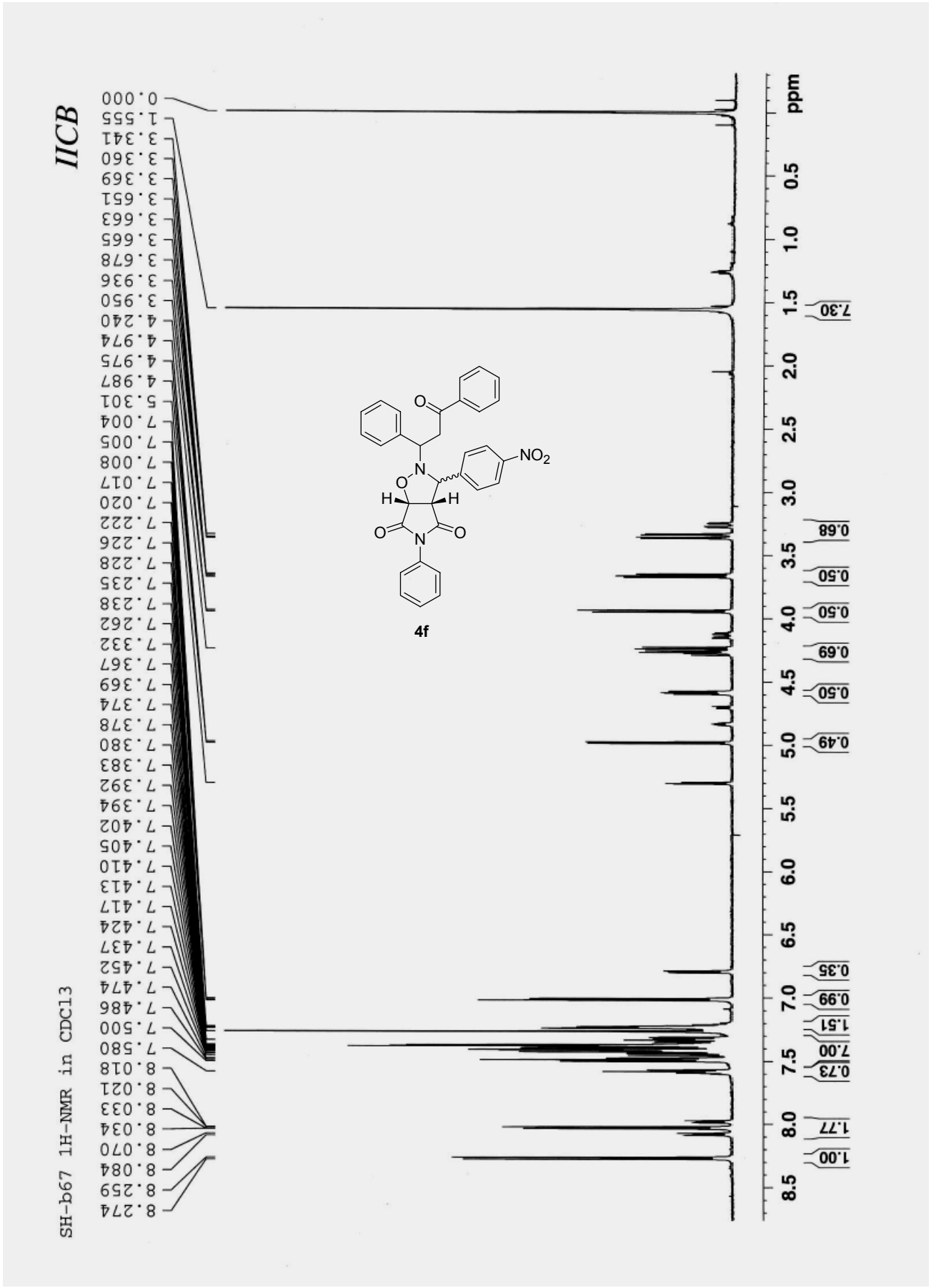
^{1}H NMR Spectrum of 4e:



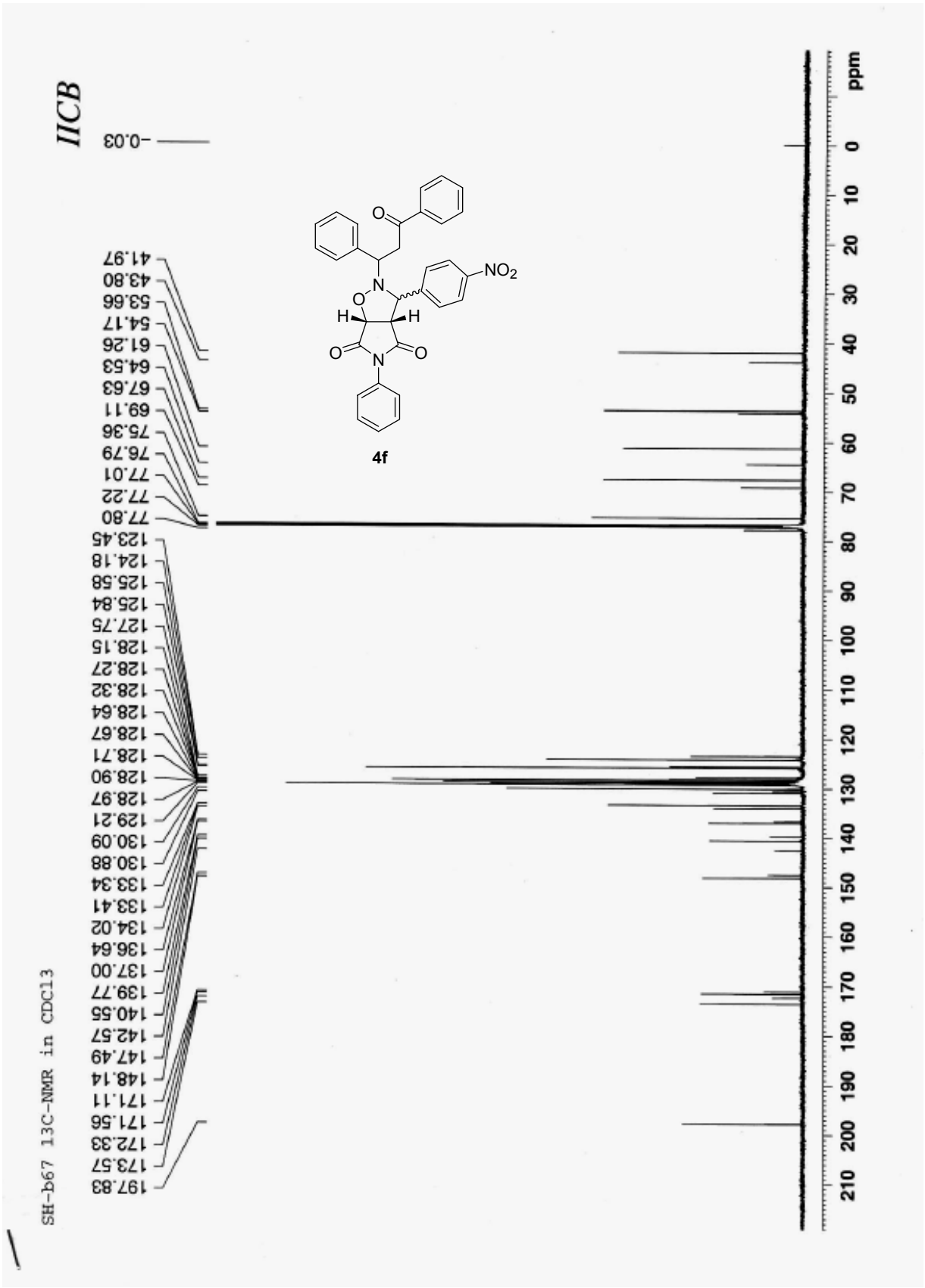
^{13}C NMR Spectrum of 4e:



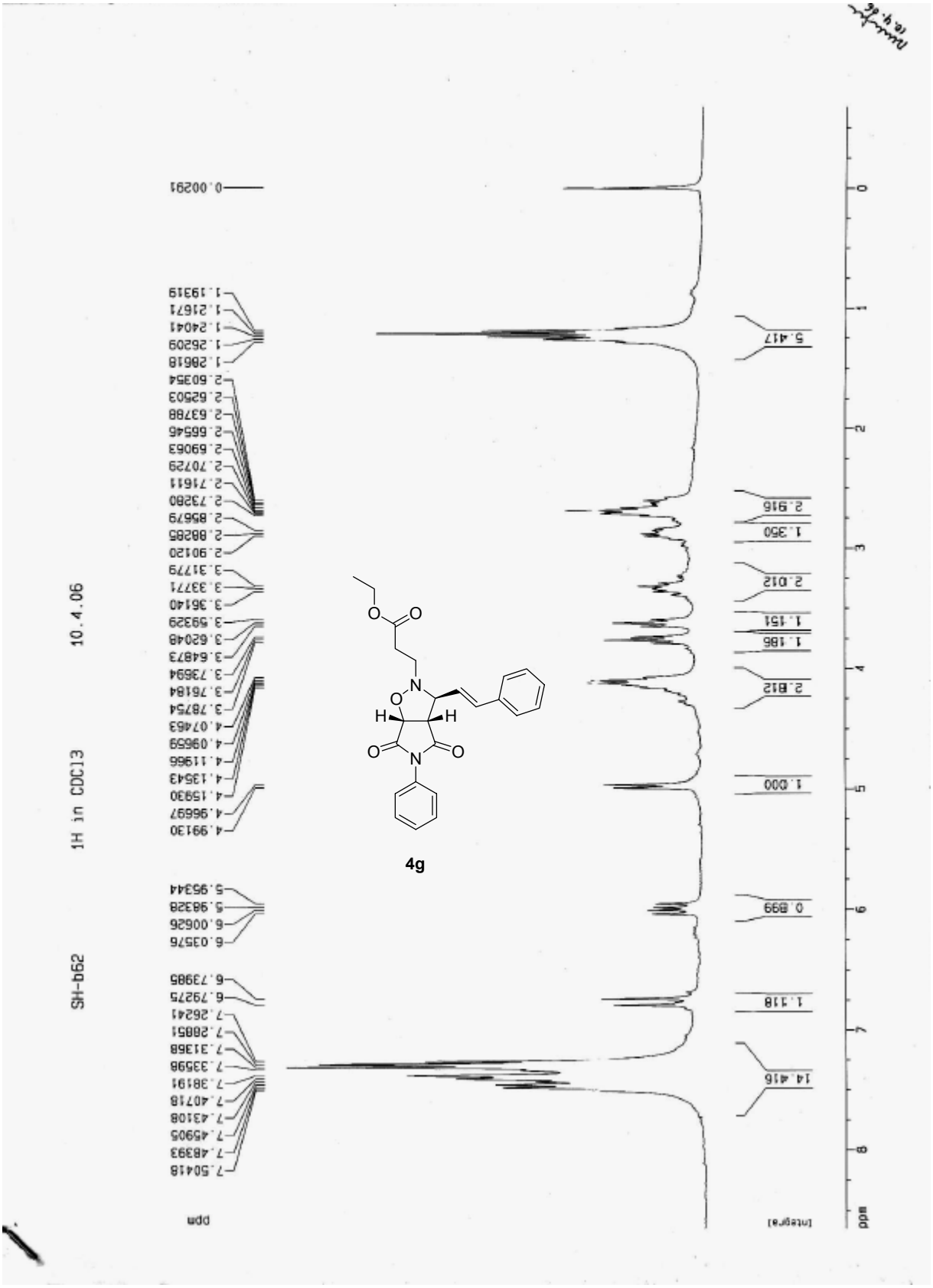
1H NMR Spectrum of 4f:



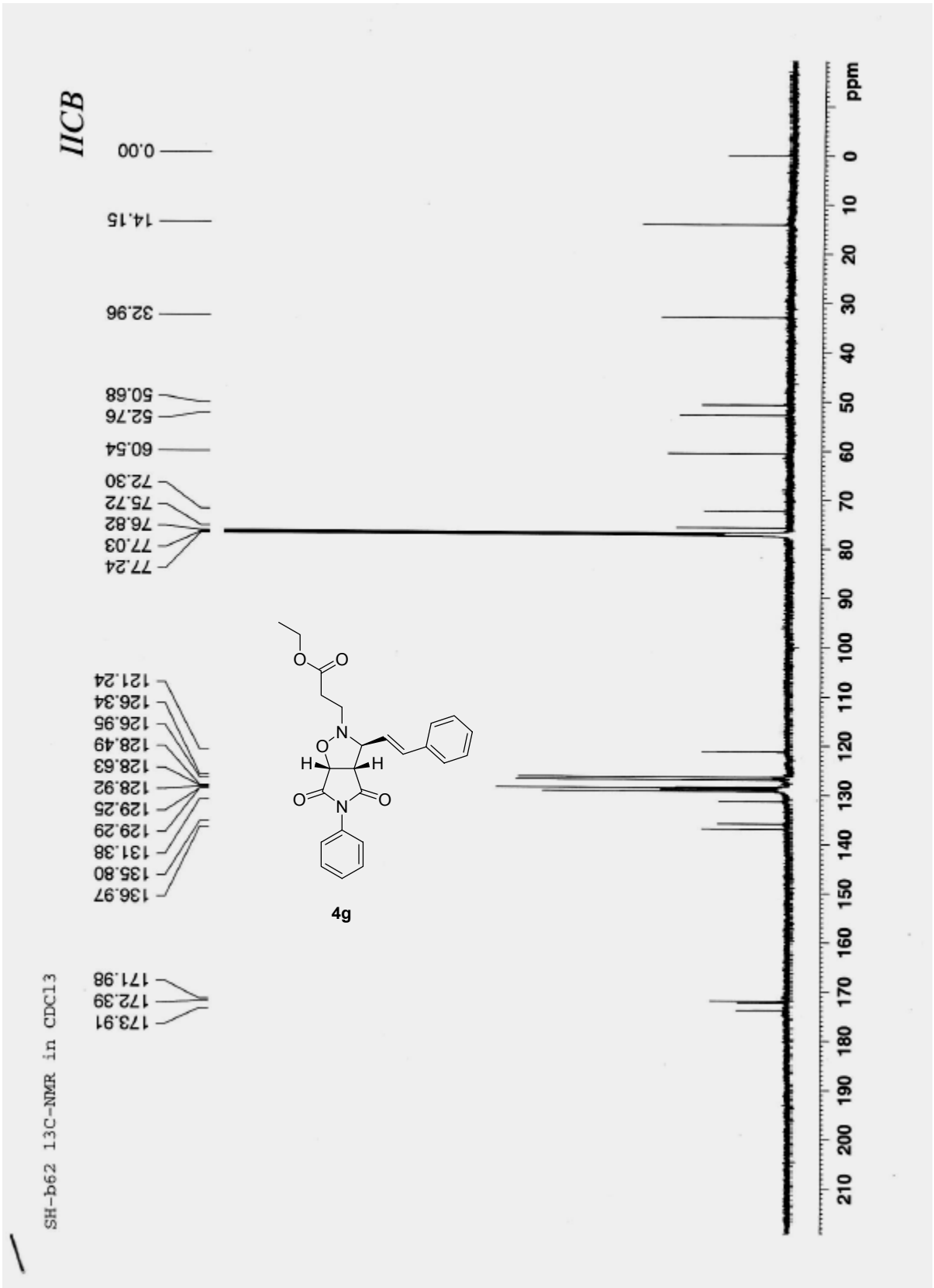
^{13}C NMR Spectrum of 4f:



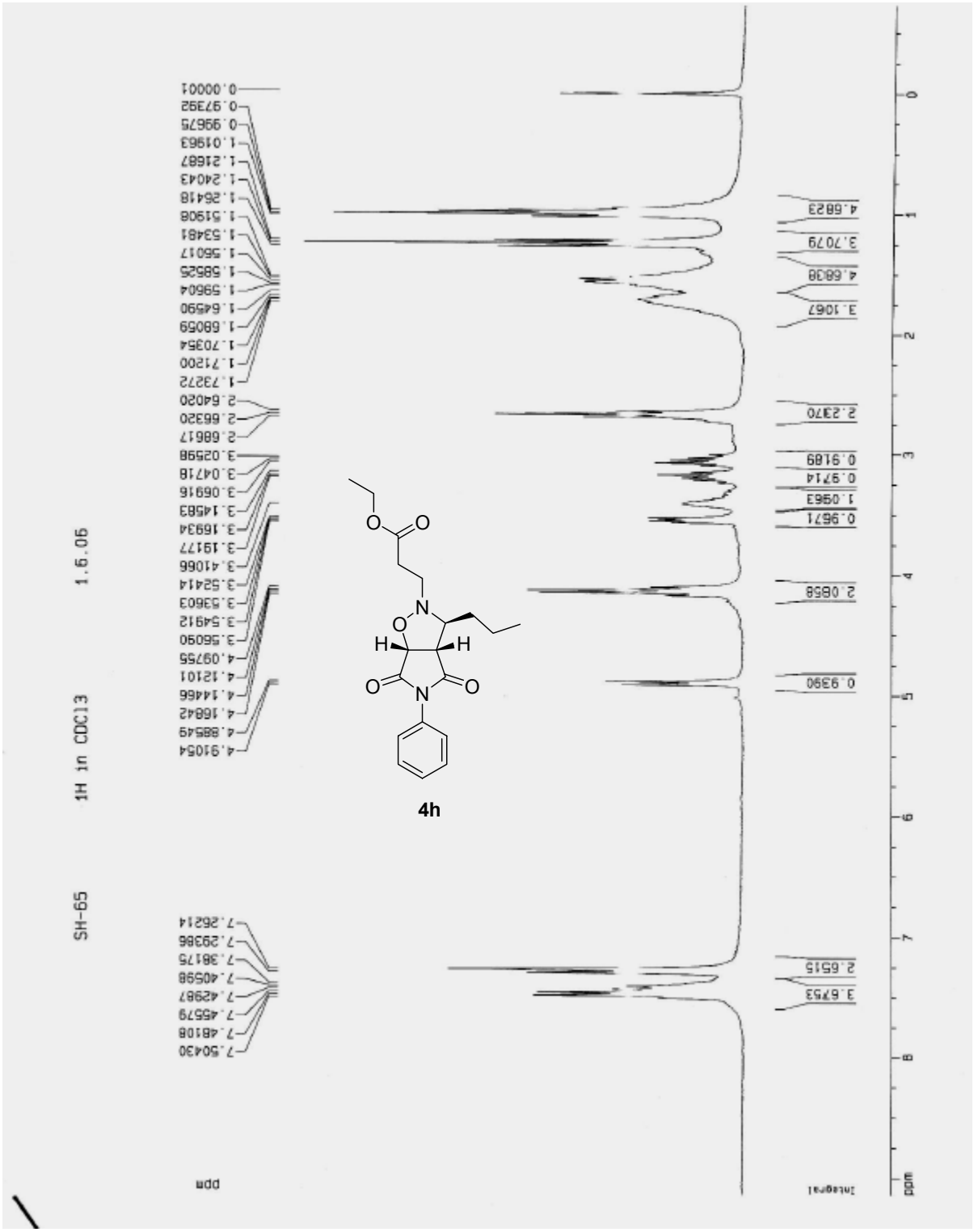
^{1}H NMR Spectrum of 4g:



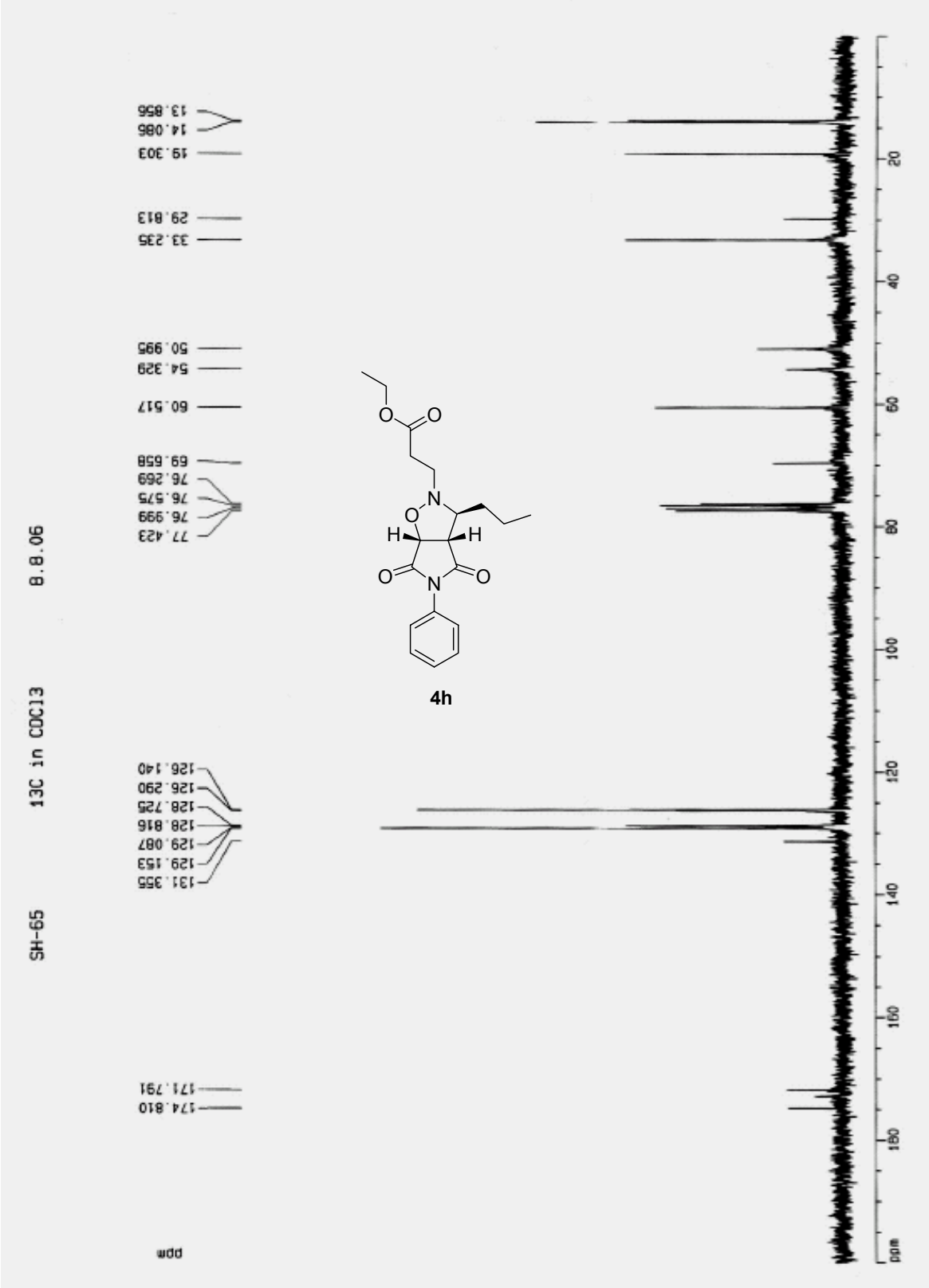
^{13}C NMR Spectrum of 4g:



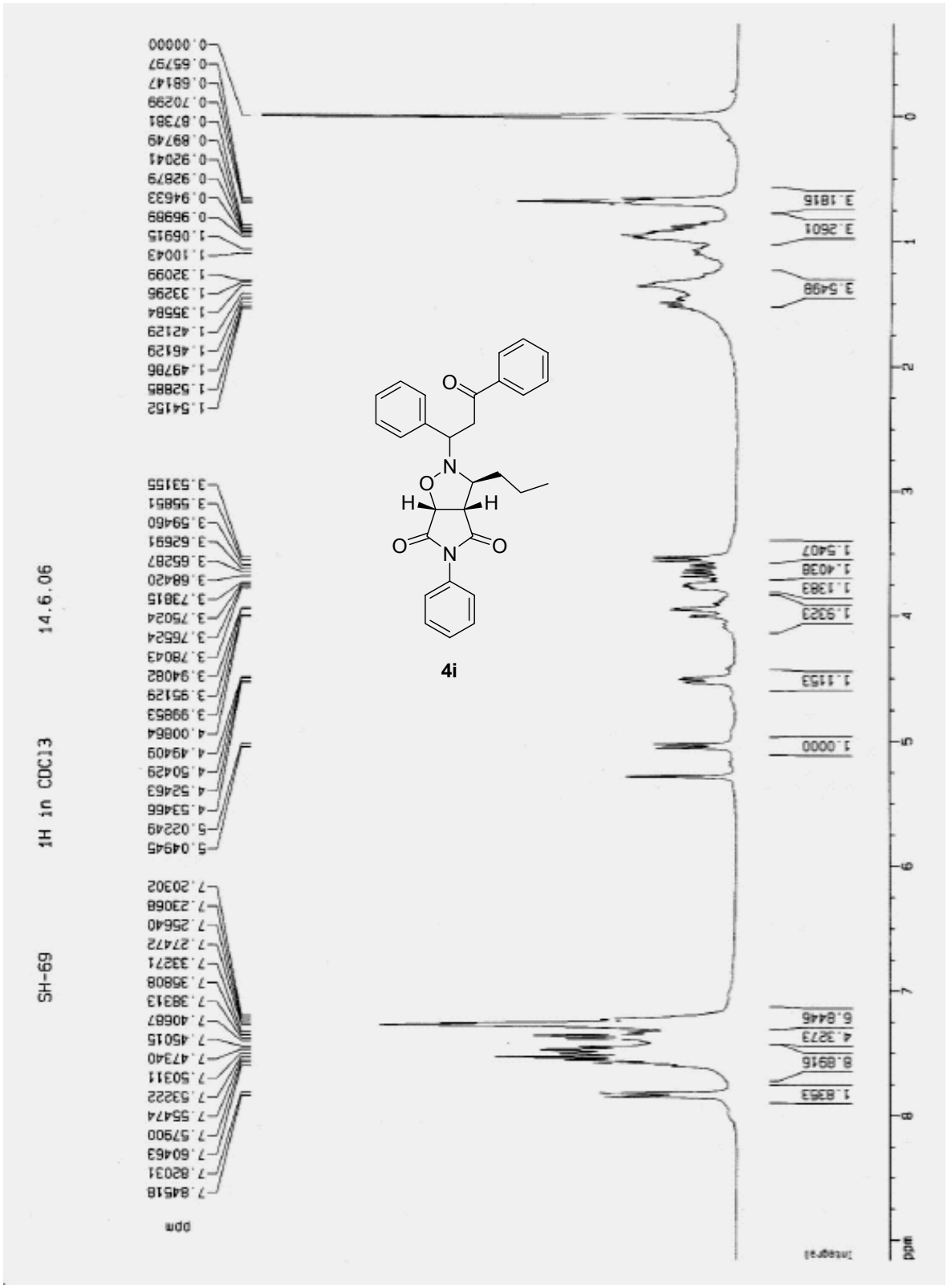
^{1}H NMR Spectrum of 4h:



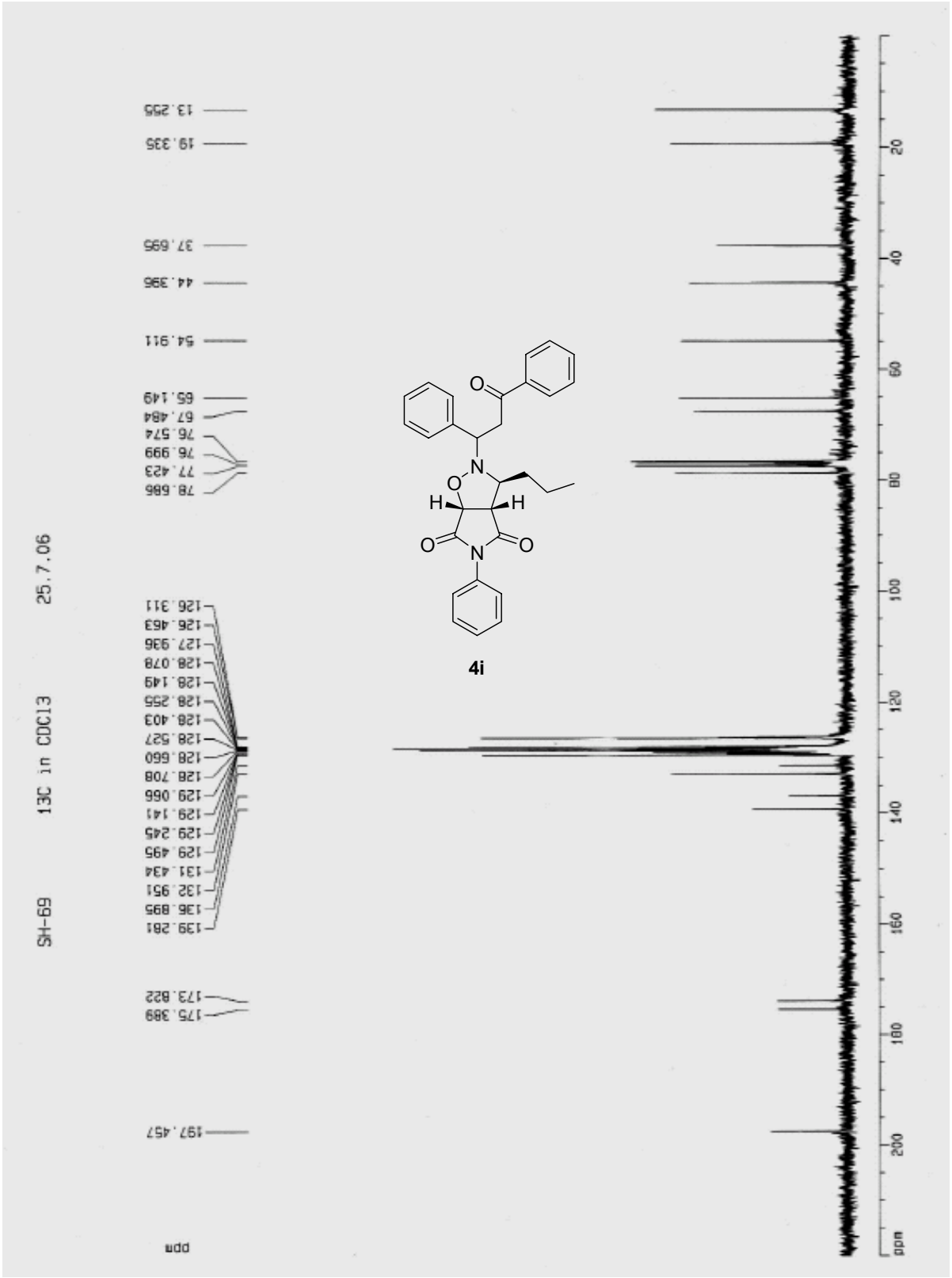
^{13}C NMR Spectrum of 4h:



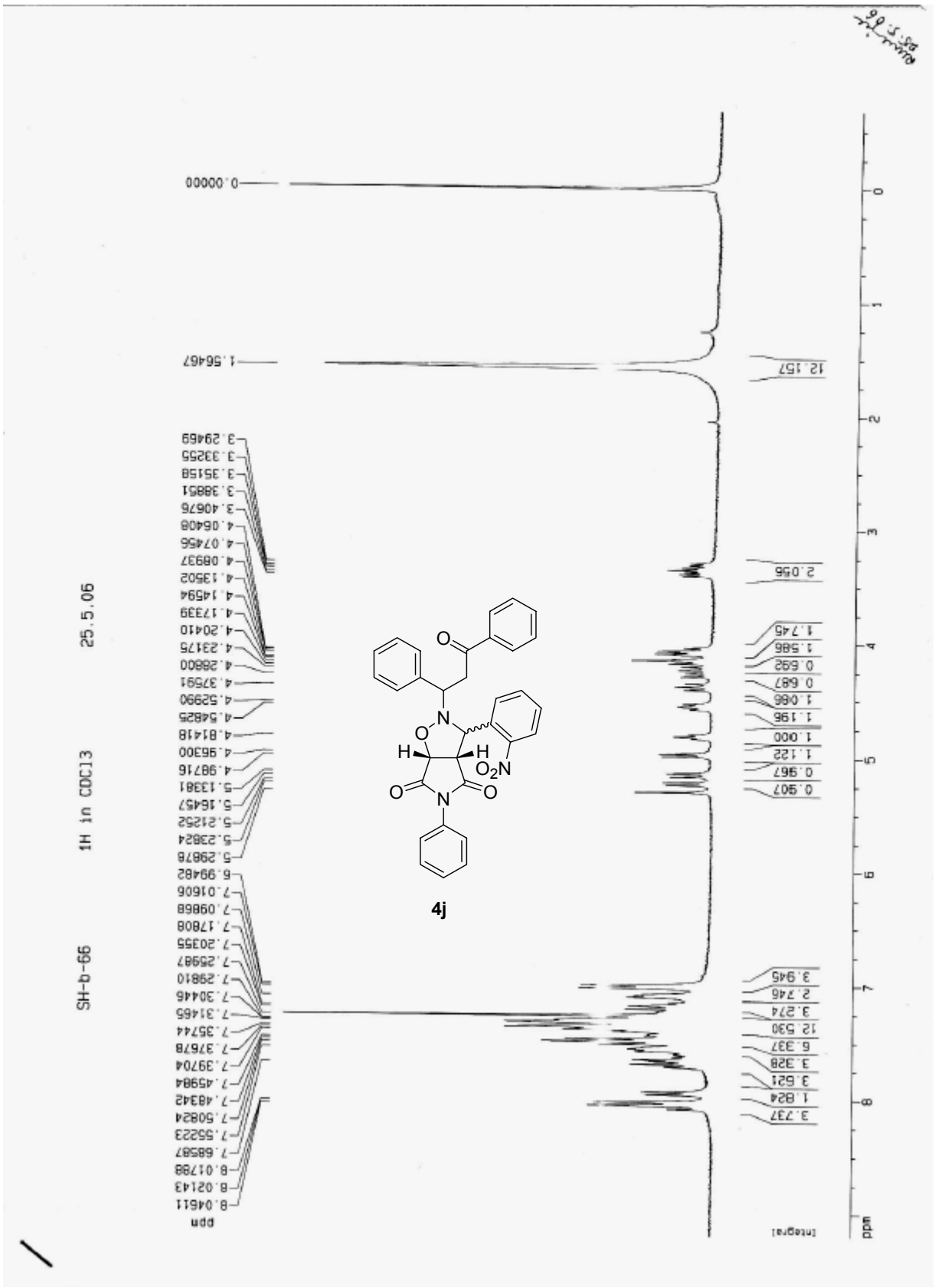
^{1}H NMR Spectrum of 4i:



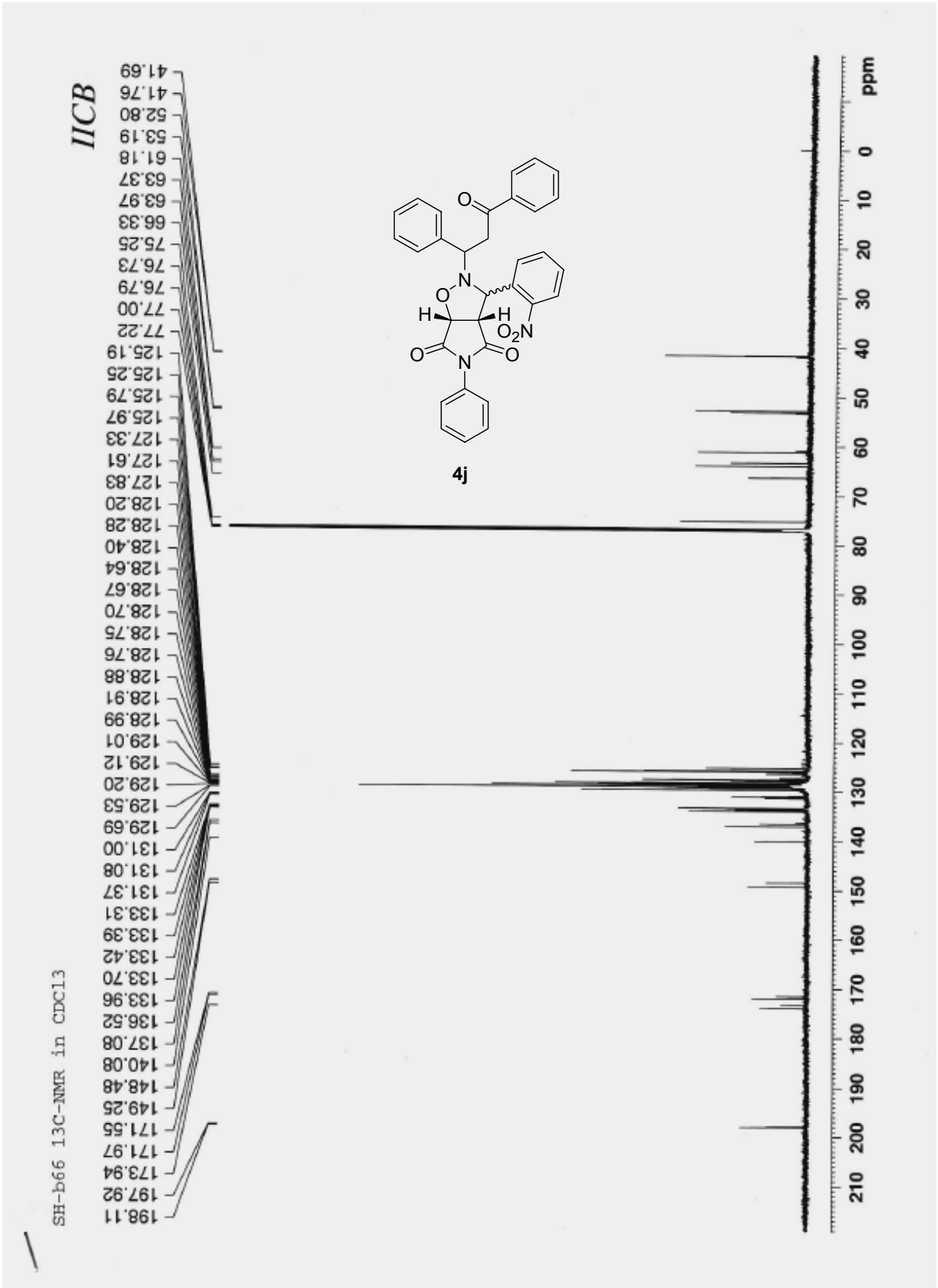
^{13}C NMR Spectrum of 4i:



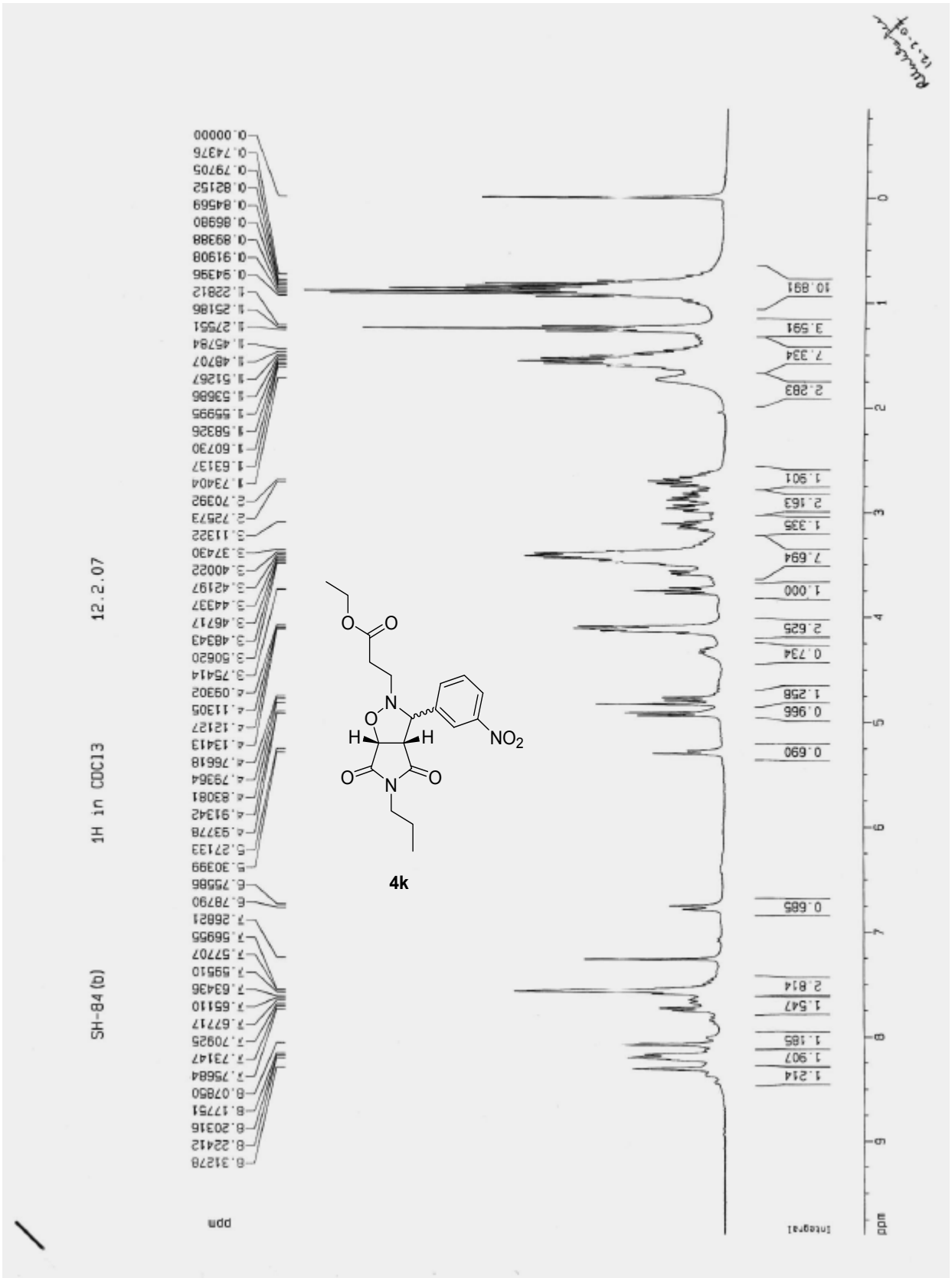
^{1}H NMR Spectrum of 4j:



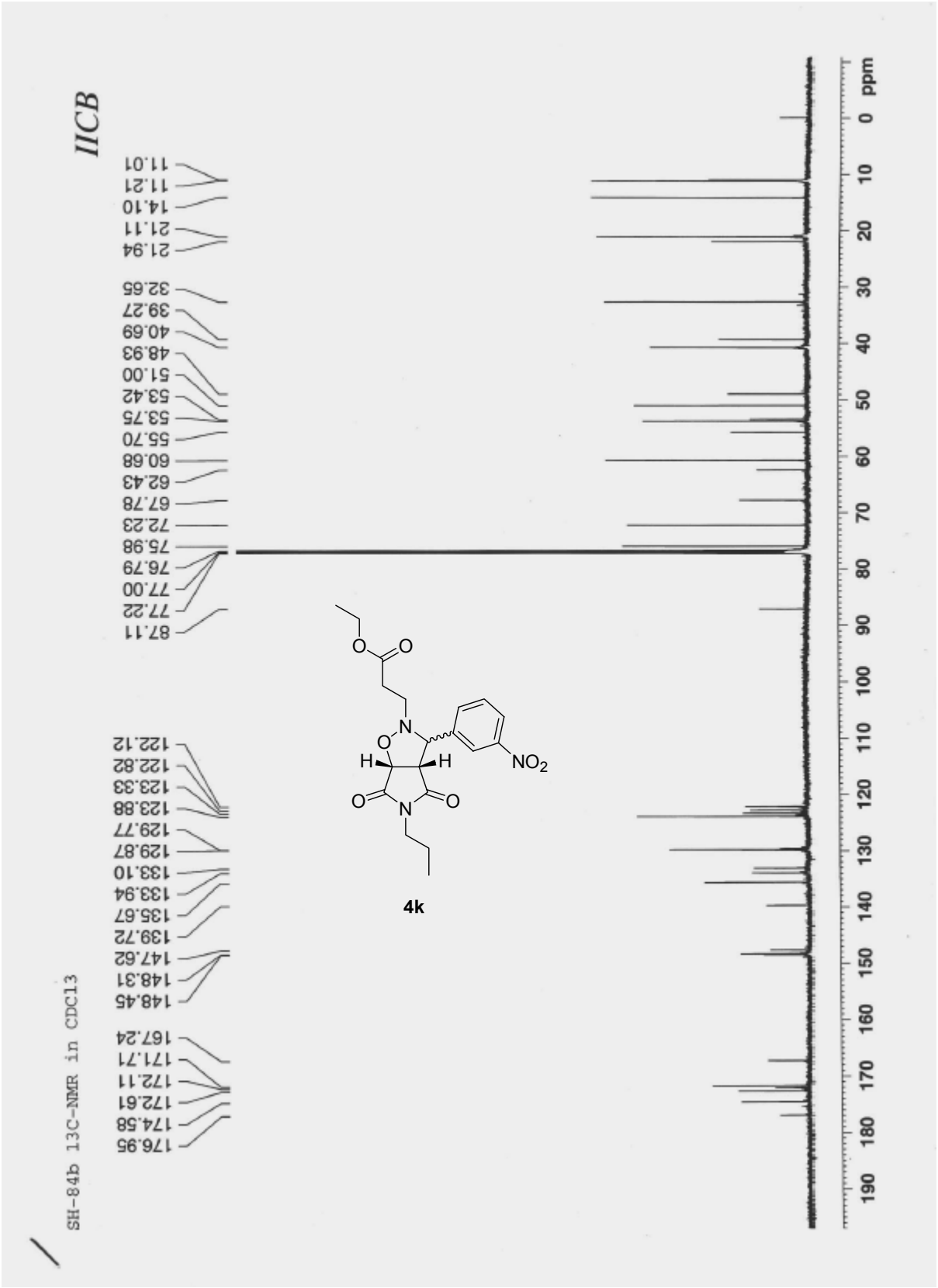
^{13}C NMR Spectrum of 4j:



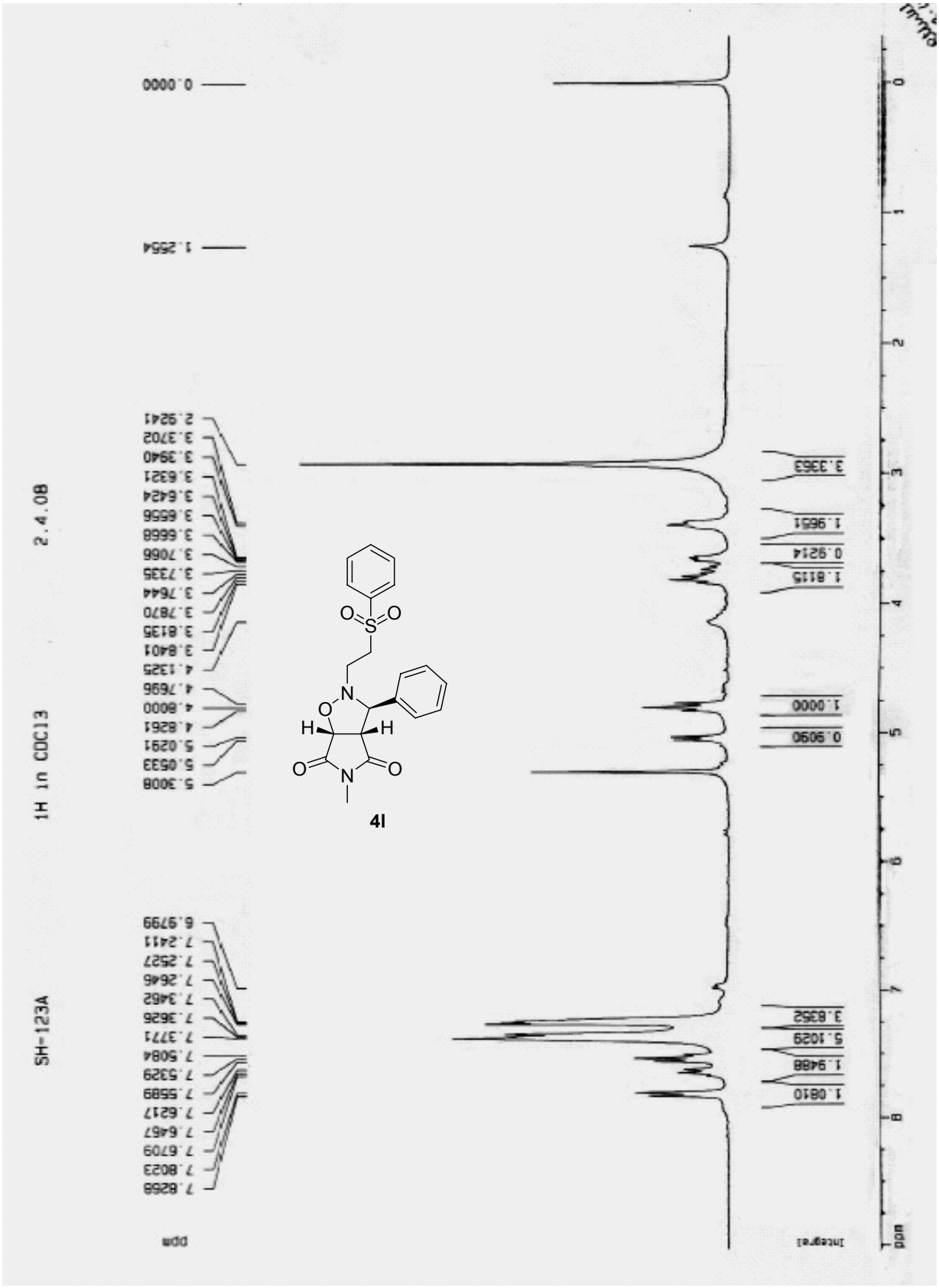
^{1}H NMR Spectrum of 4k:



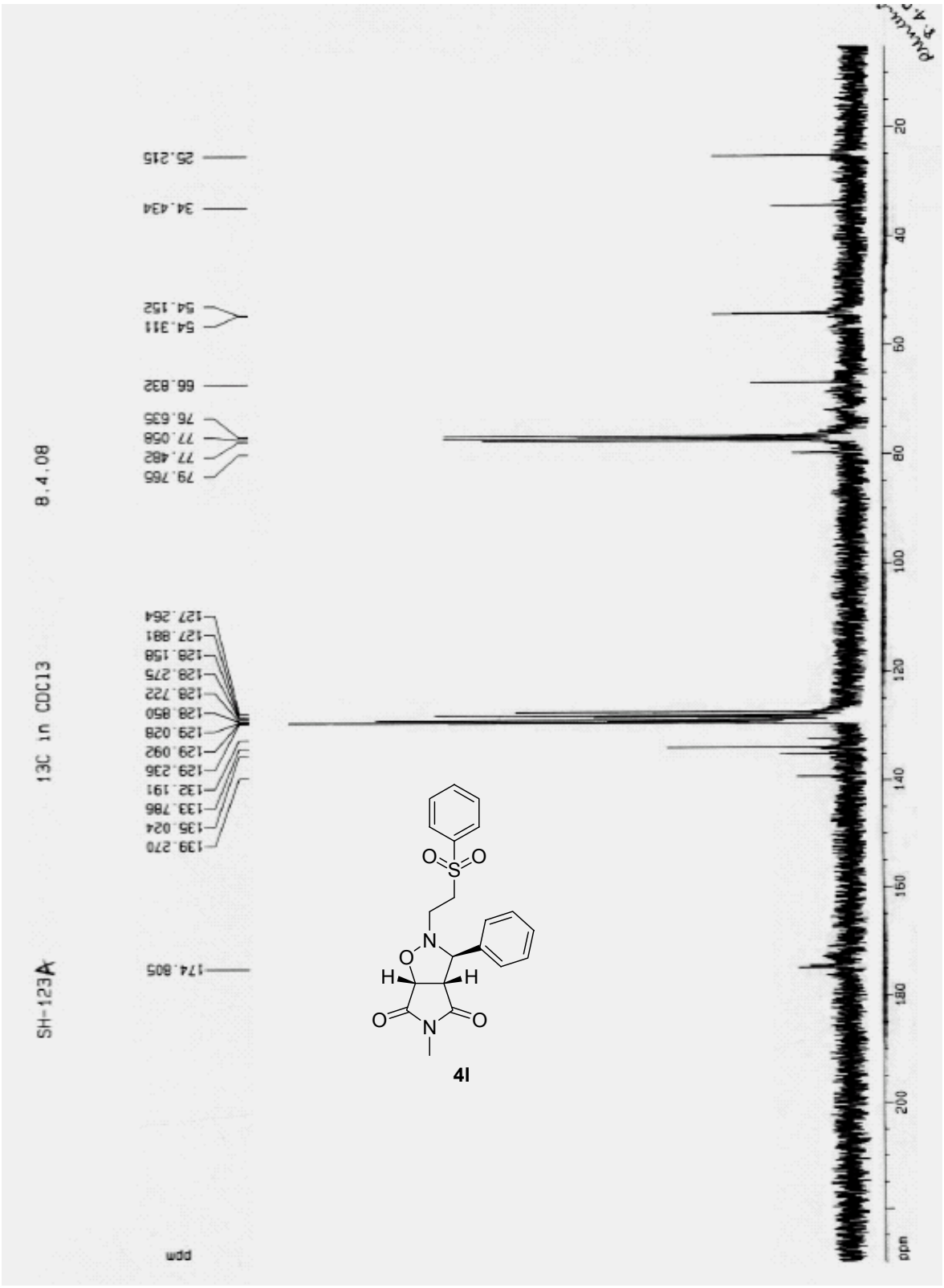
^{13}C NMR Spectrum of 4k:



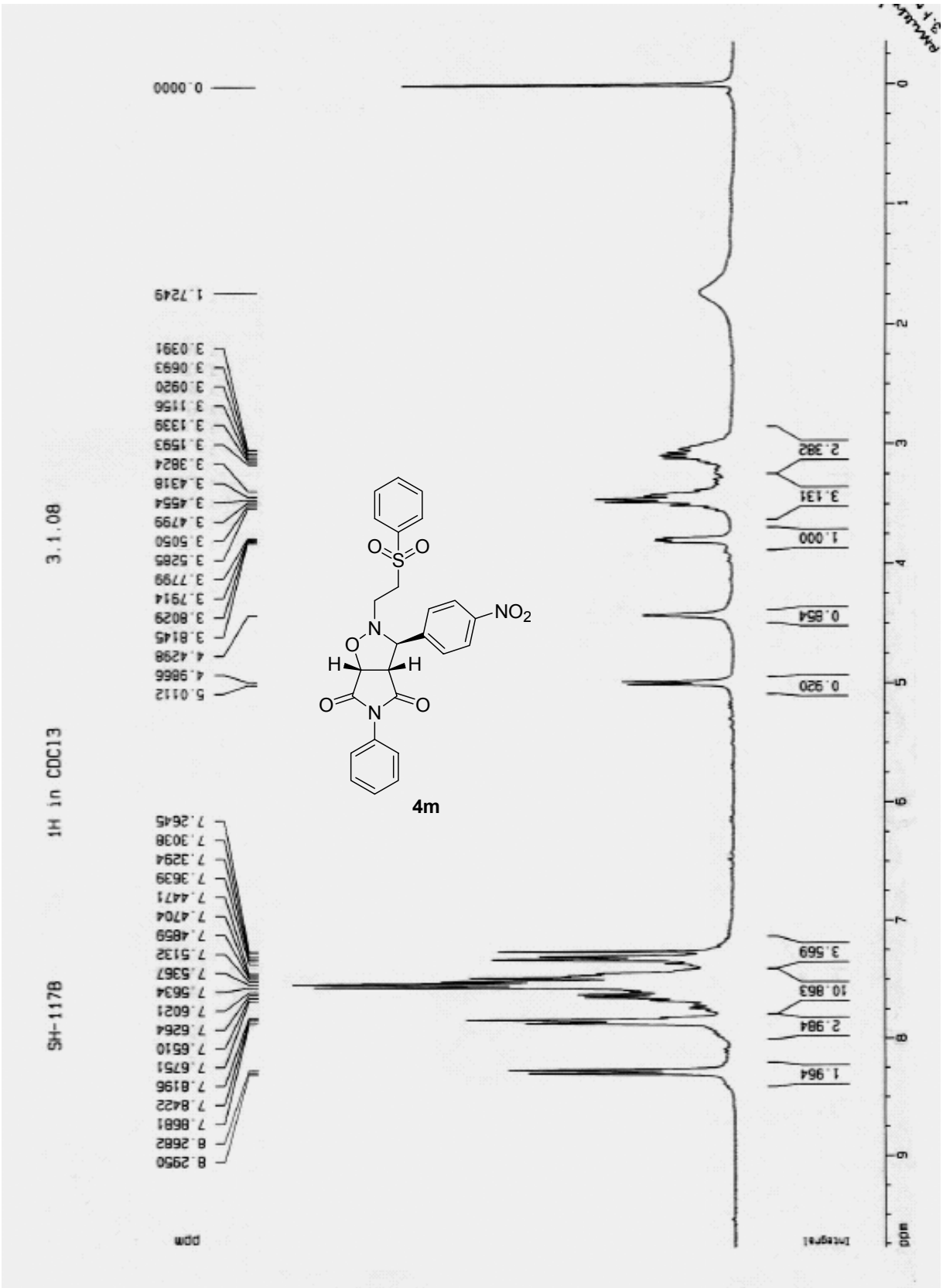
^{1}H NMR Spectrum of 4l:



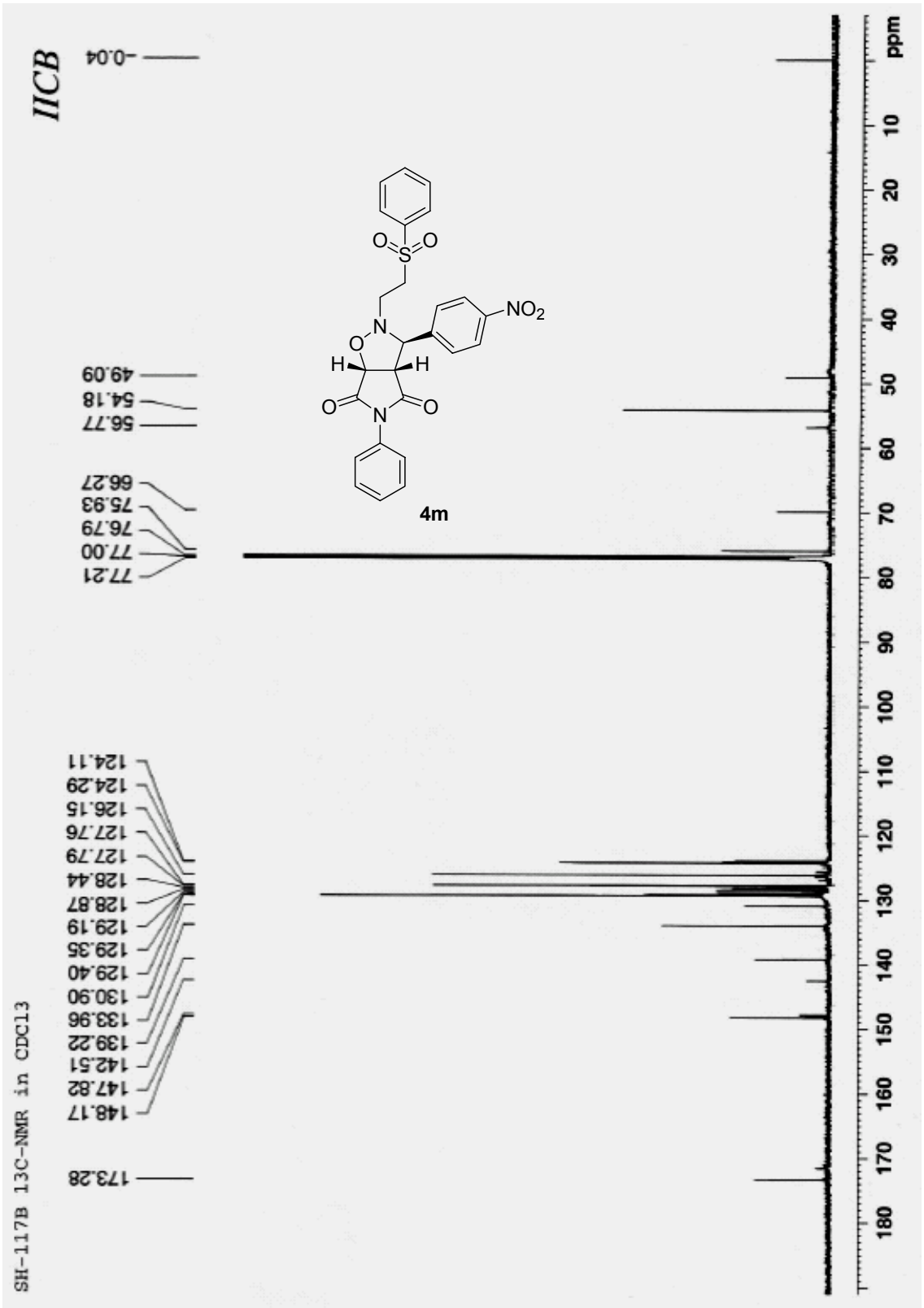
^{13}C NMR Spectrum of 4l:



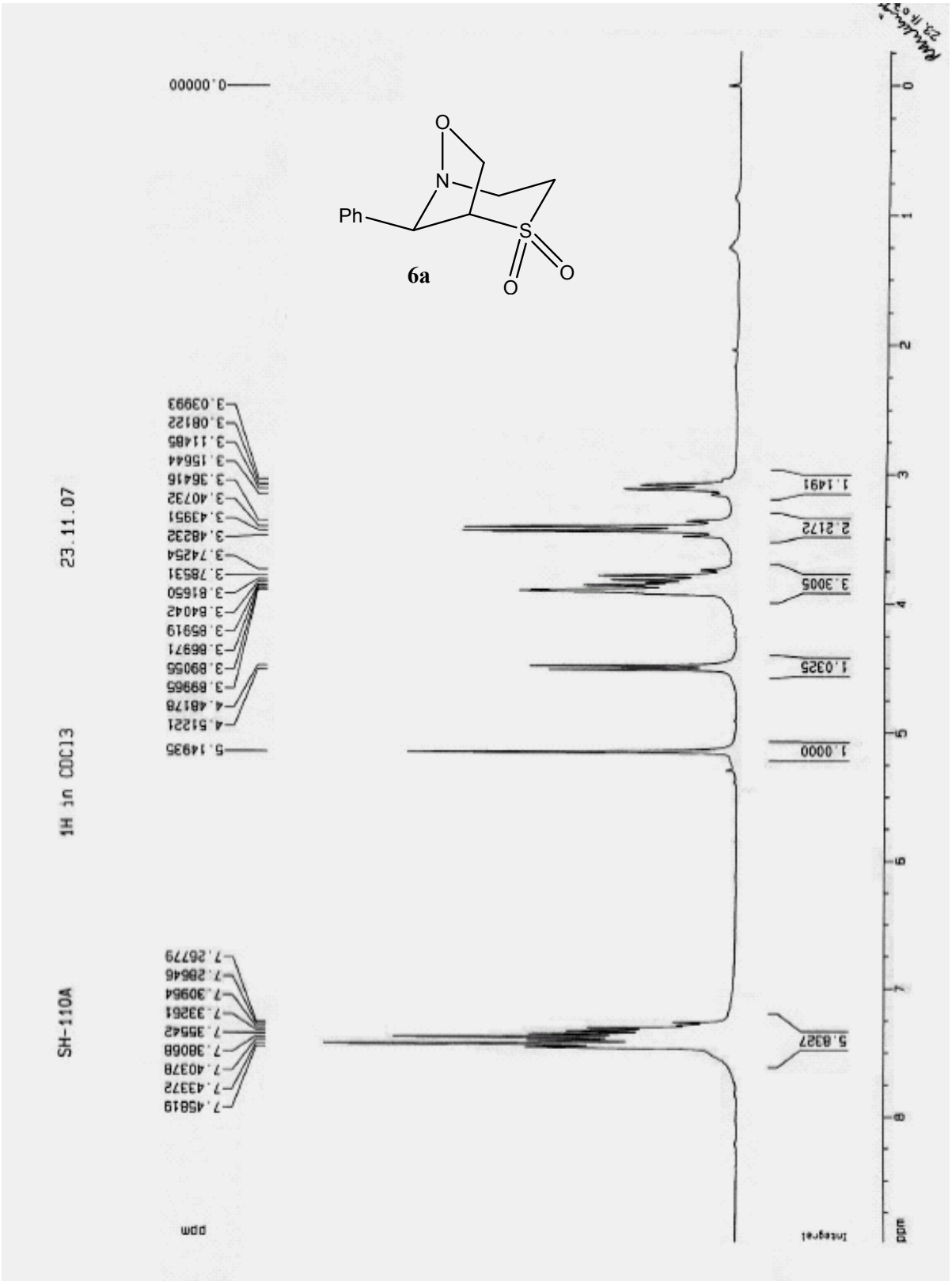
^{1}H NMR Spectrum of 4m:



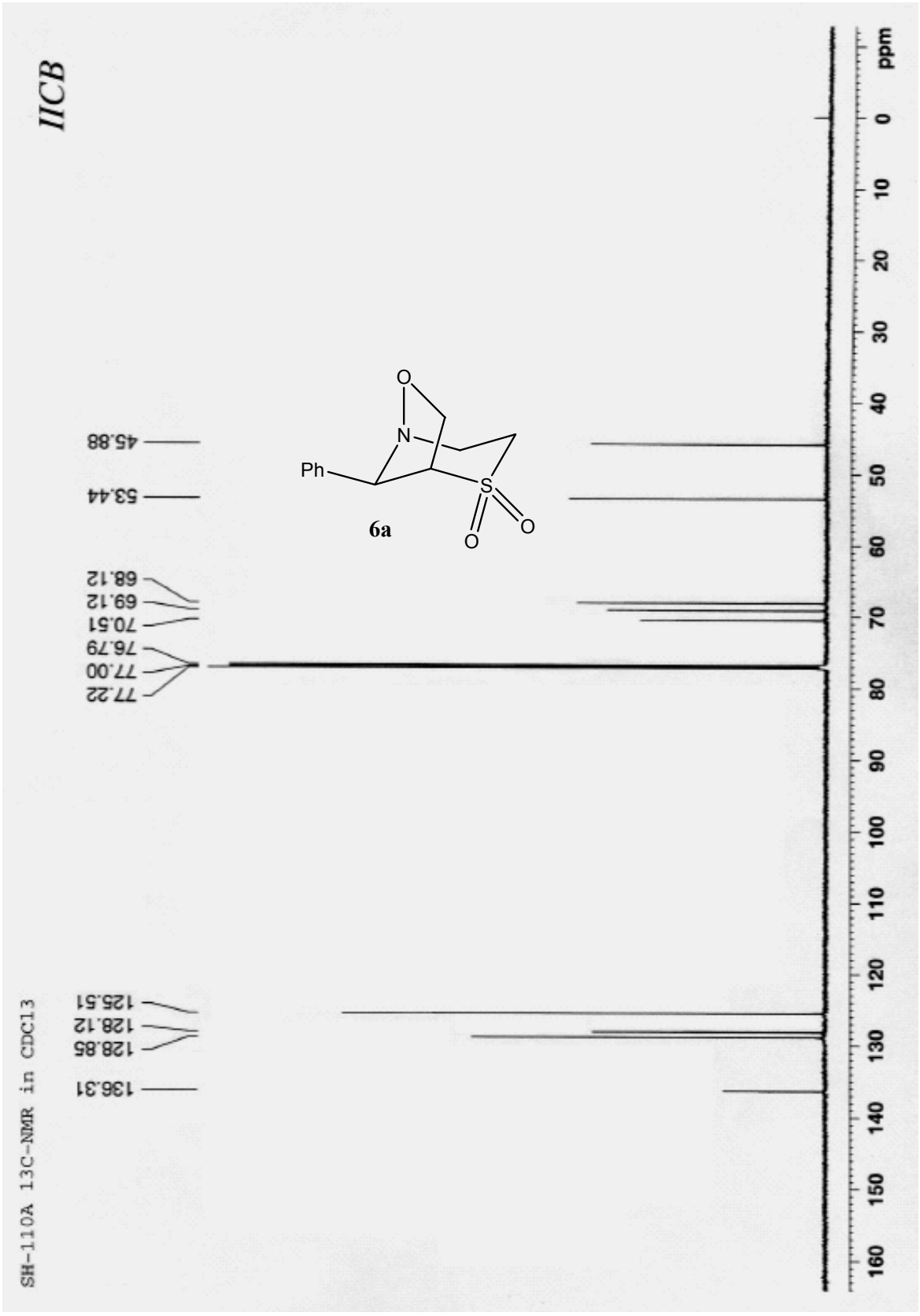
^{13}C NMR Spectrum of 4m:



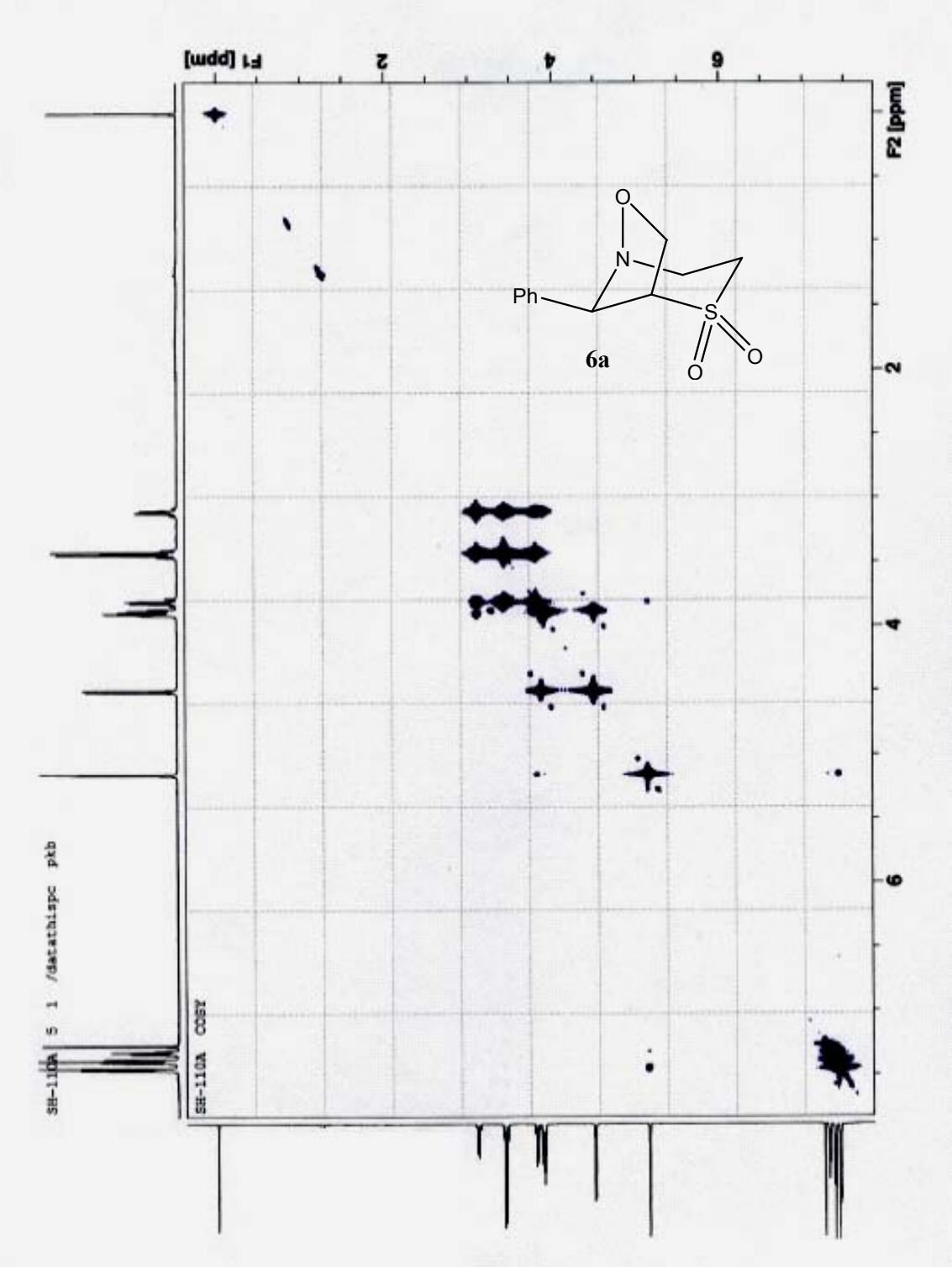
^{1}H NMR Spectrum of 6a:



^{13}C NMR Spectrum of 6a:

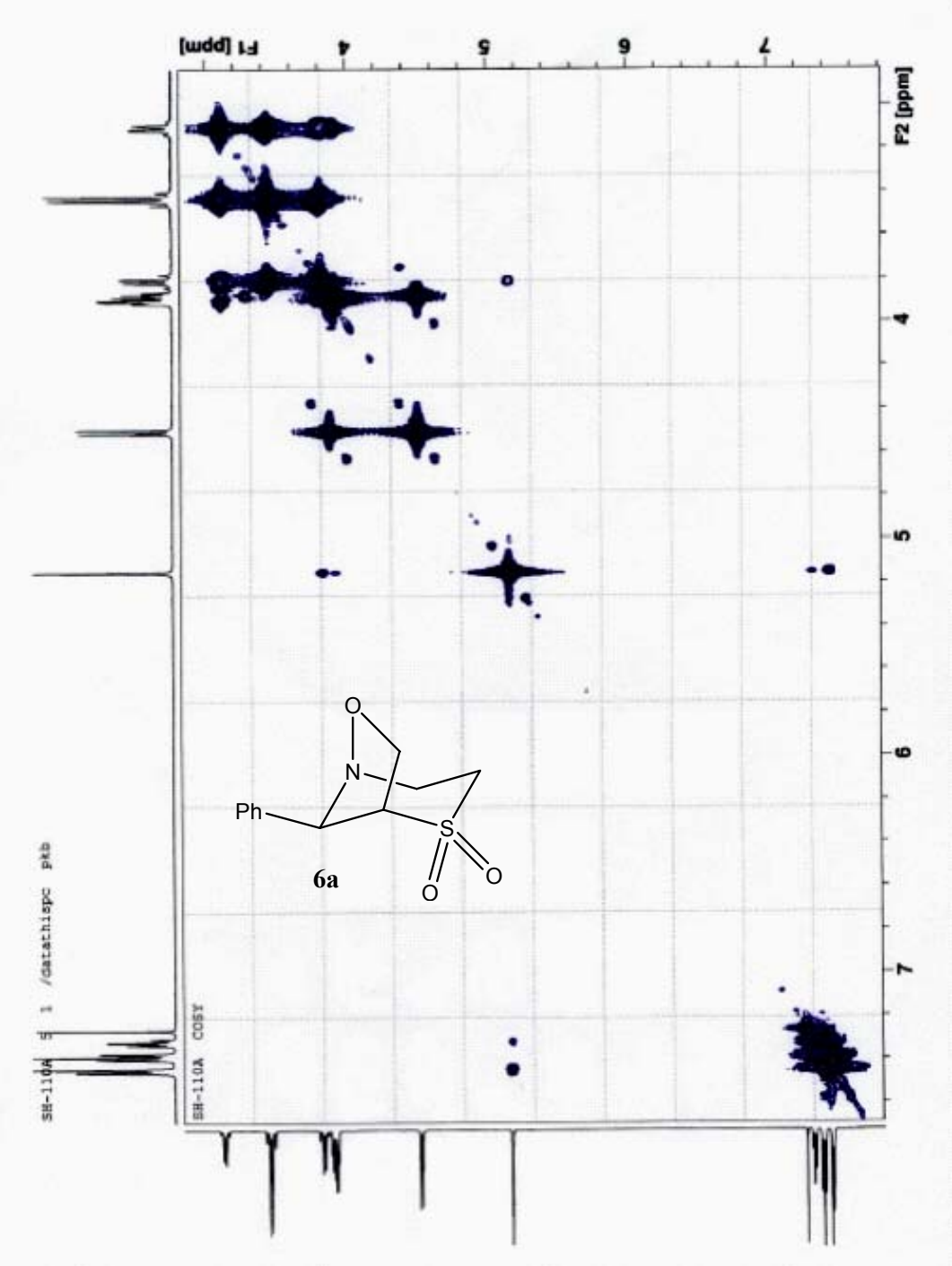


COSY Spectrum of 6a:

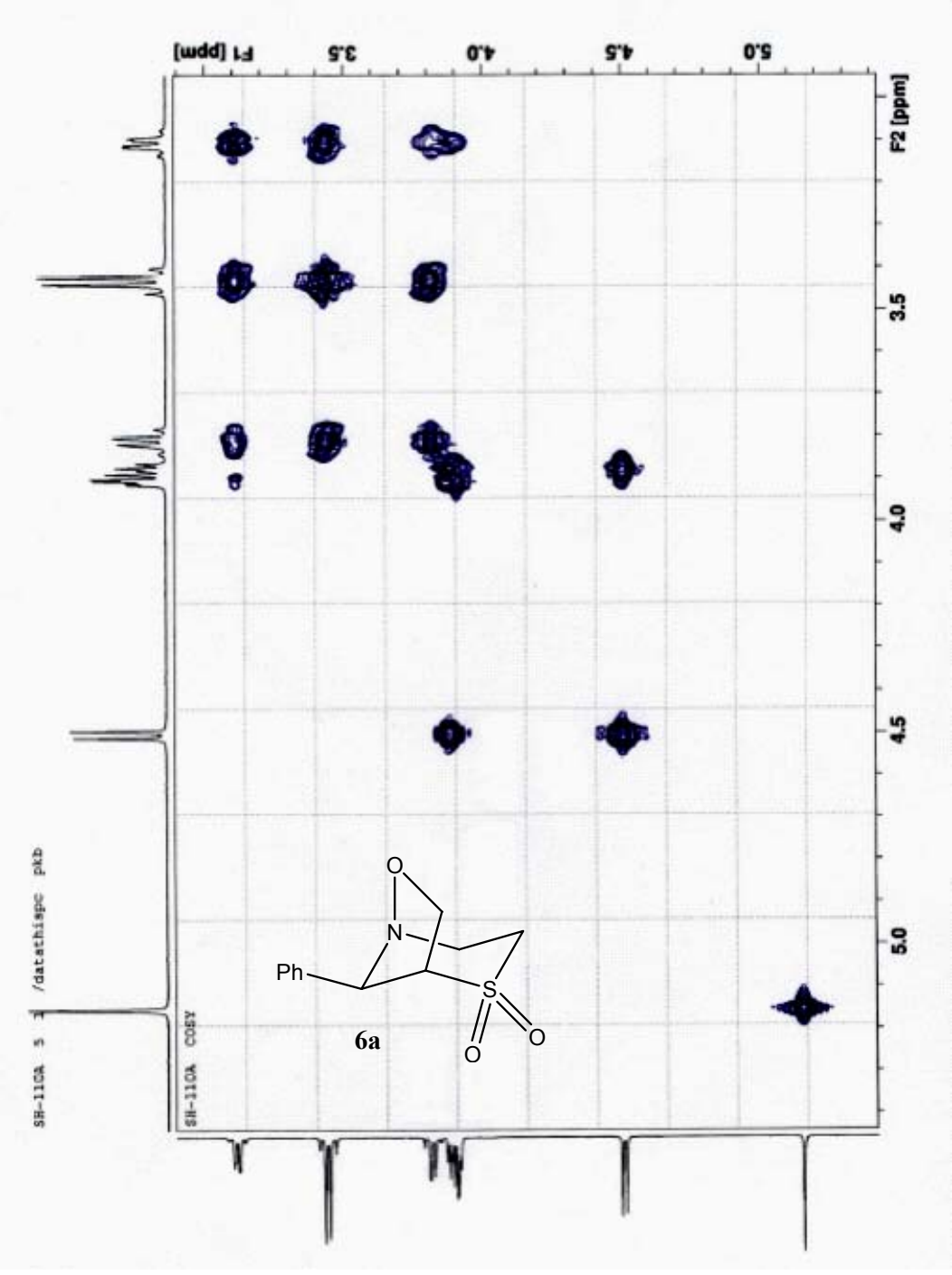


6a

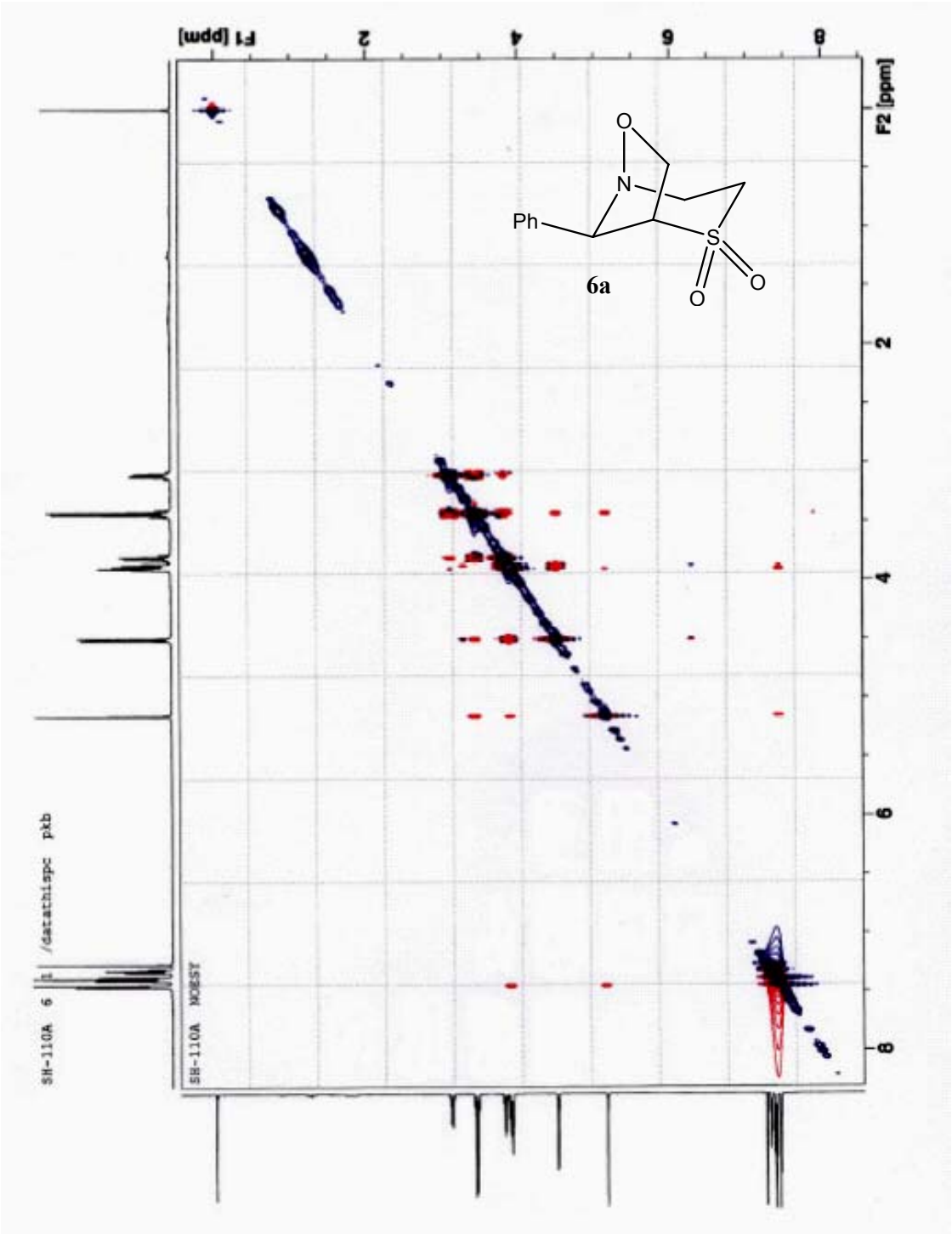
Expansion (1) of COSY Spectrum of 6a:



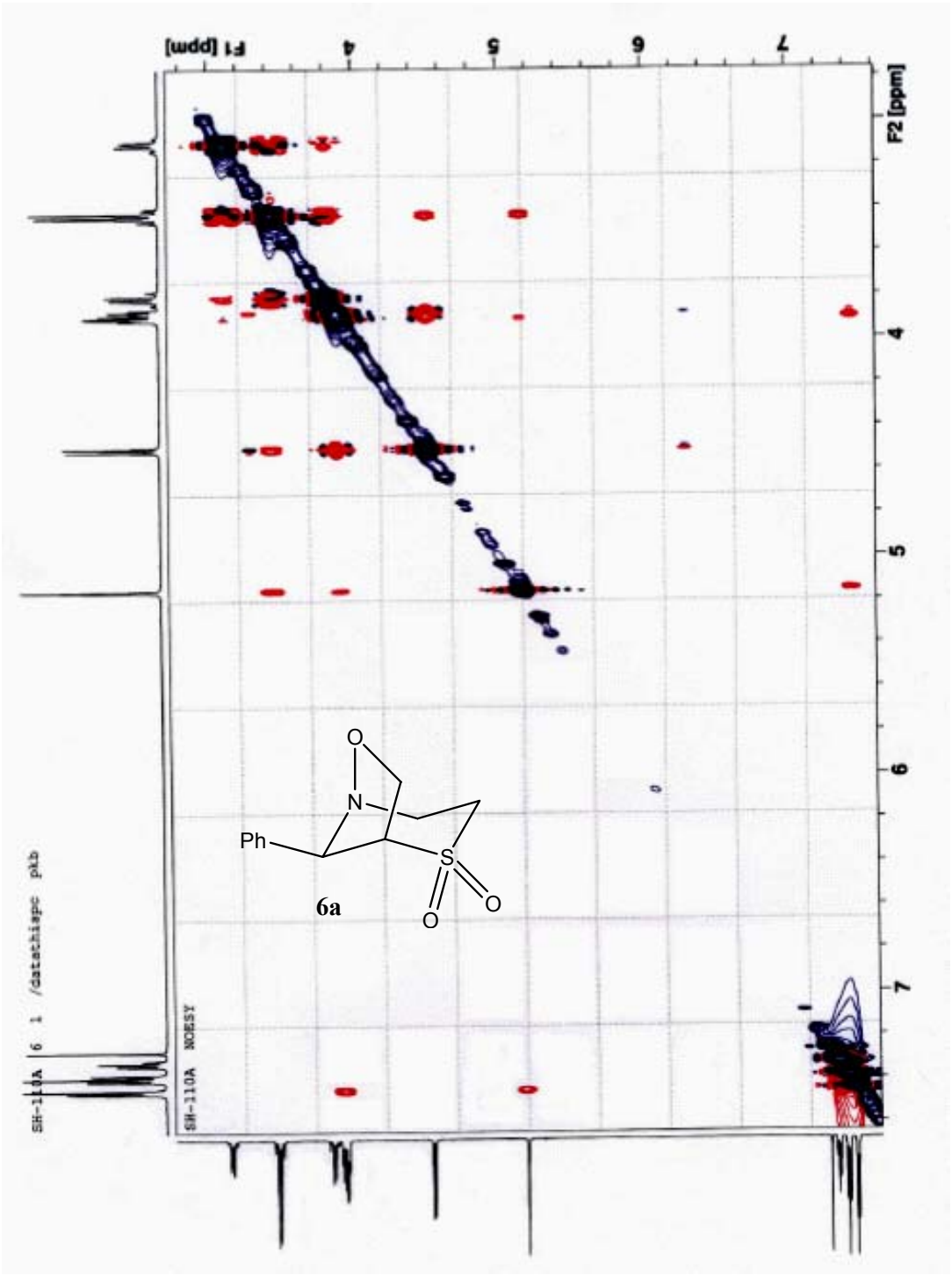
Expansion (2) of COSY Spectrum of 6a:



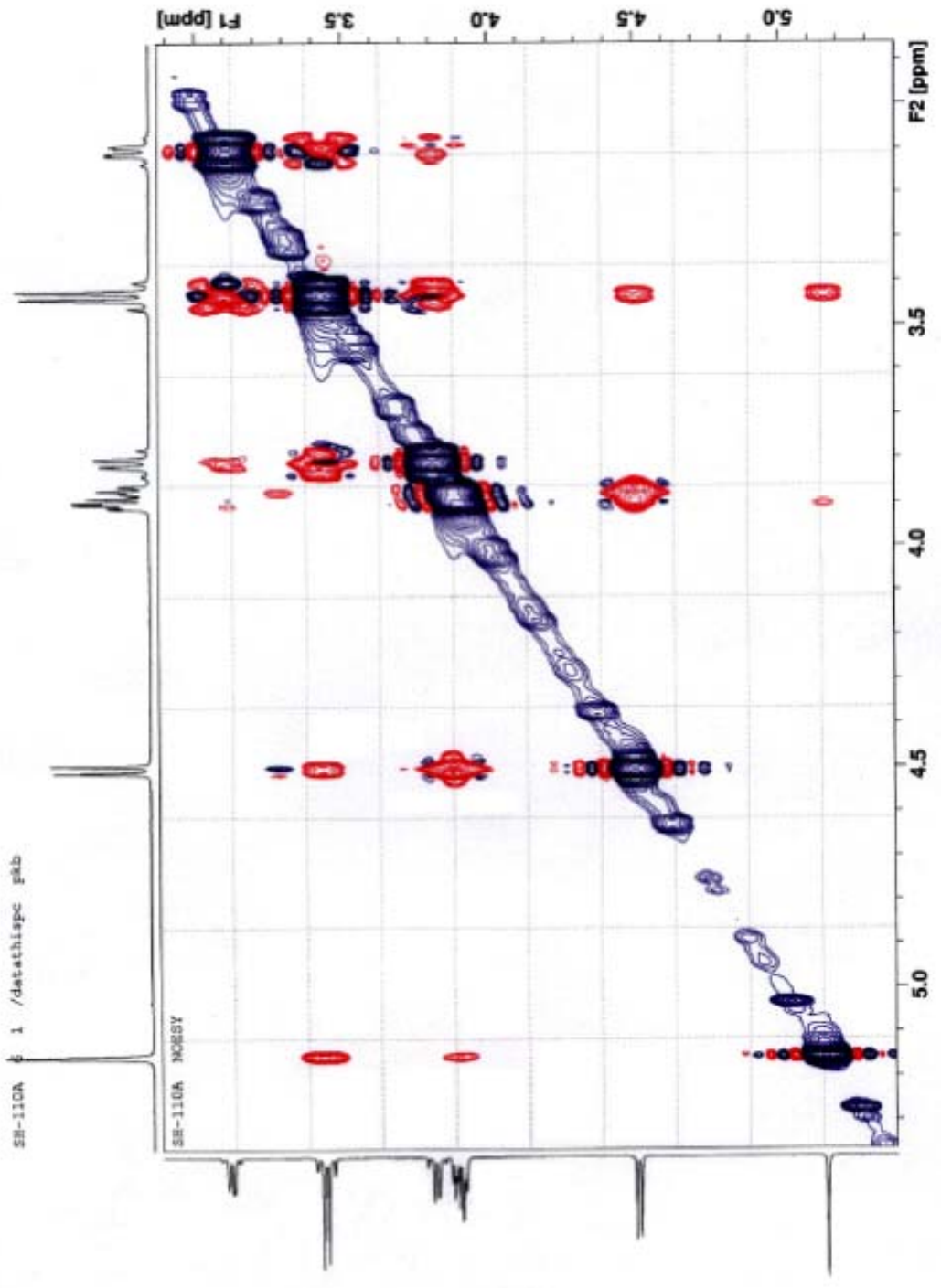
NOESY Spectrum of 6a:



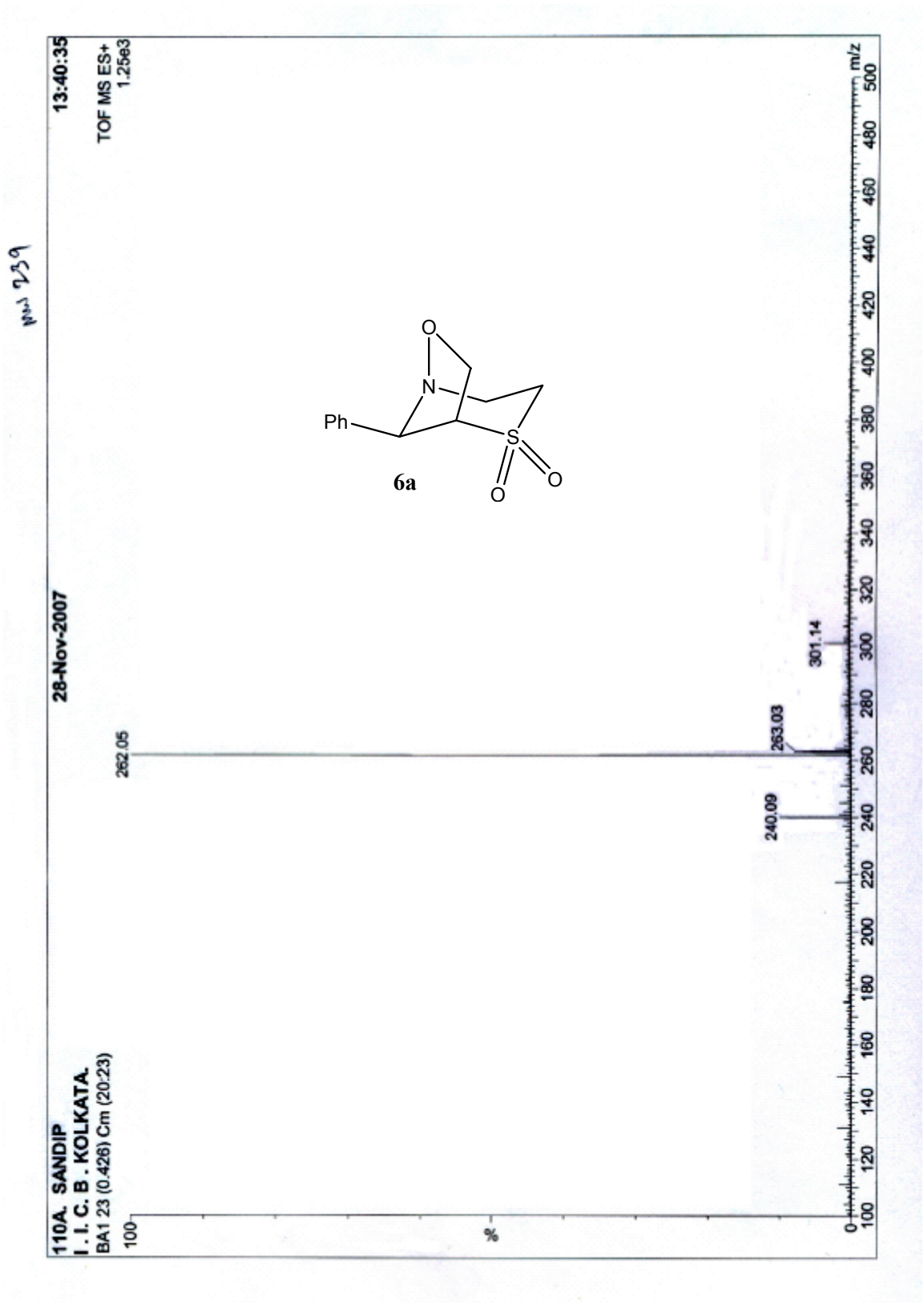
Expansion (1) of NOESY Spectrum of 6a:



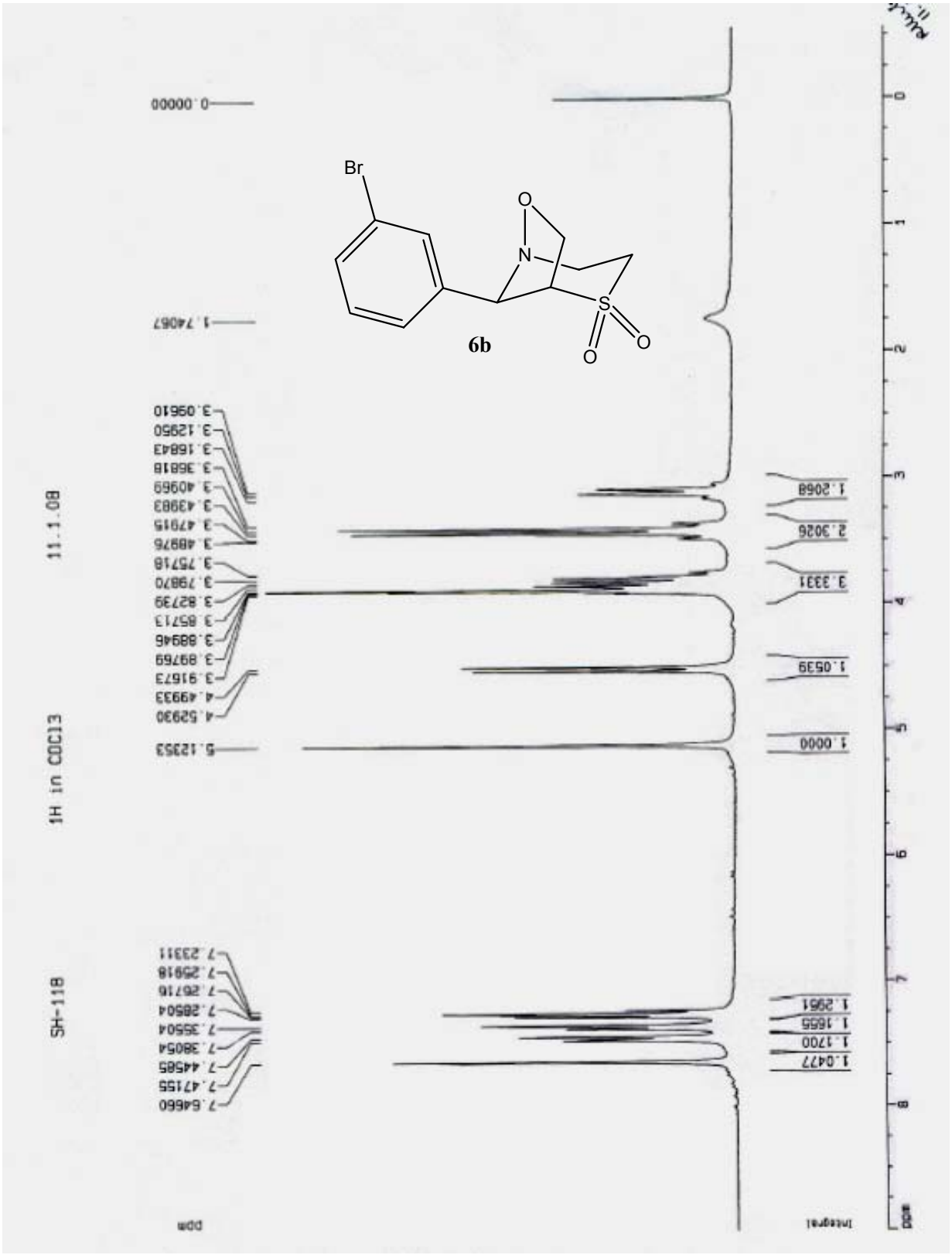
Expansion (2) of NOESY Spectrum of 6a:



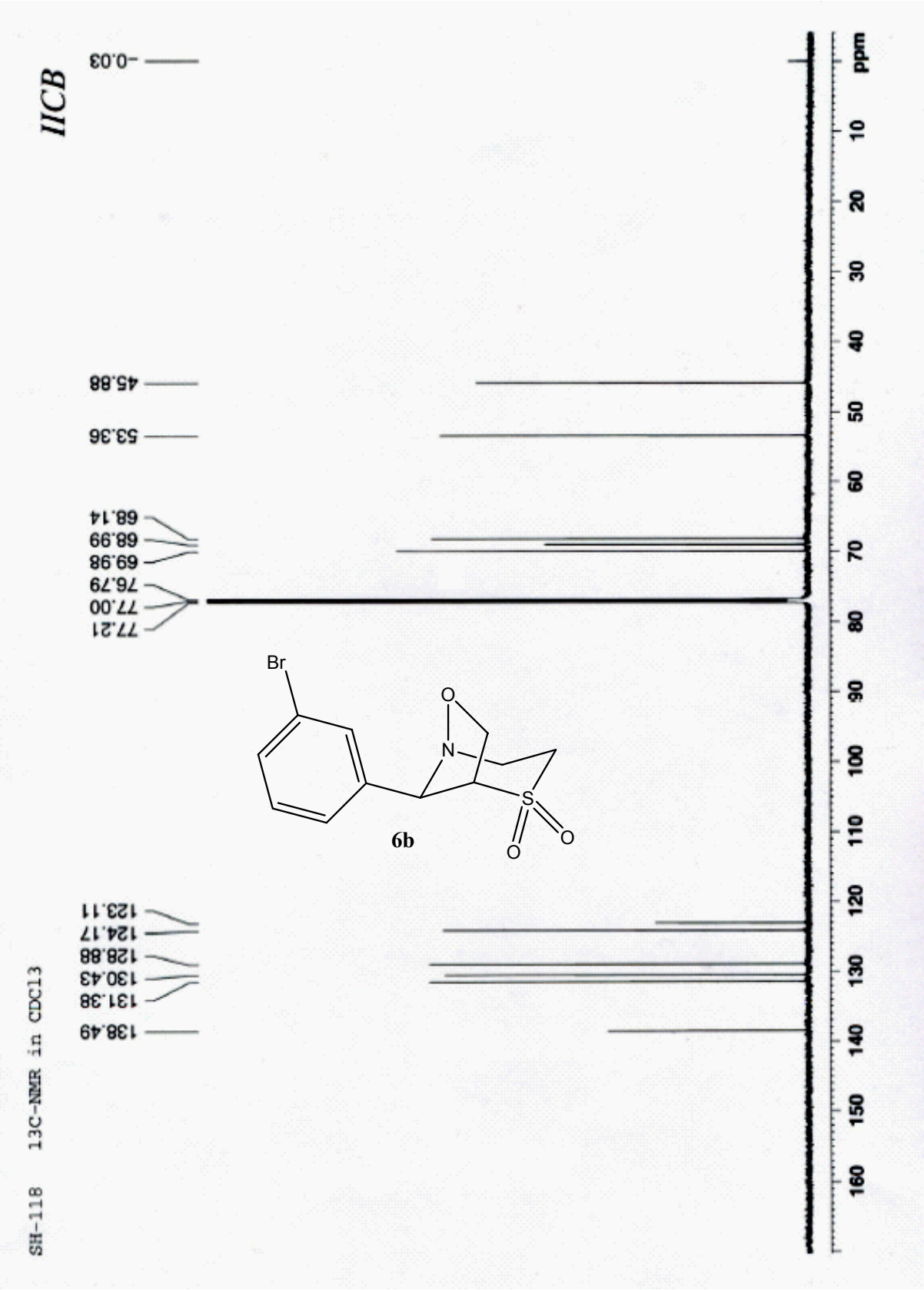
Mass Spectrum of 6a:



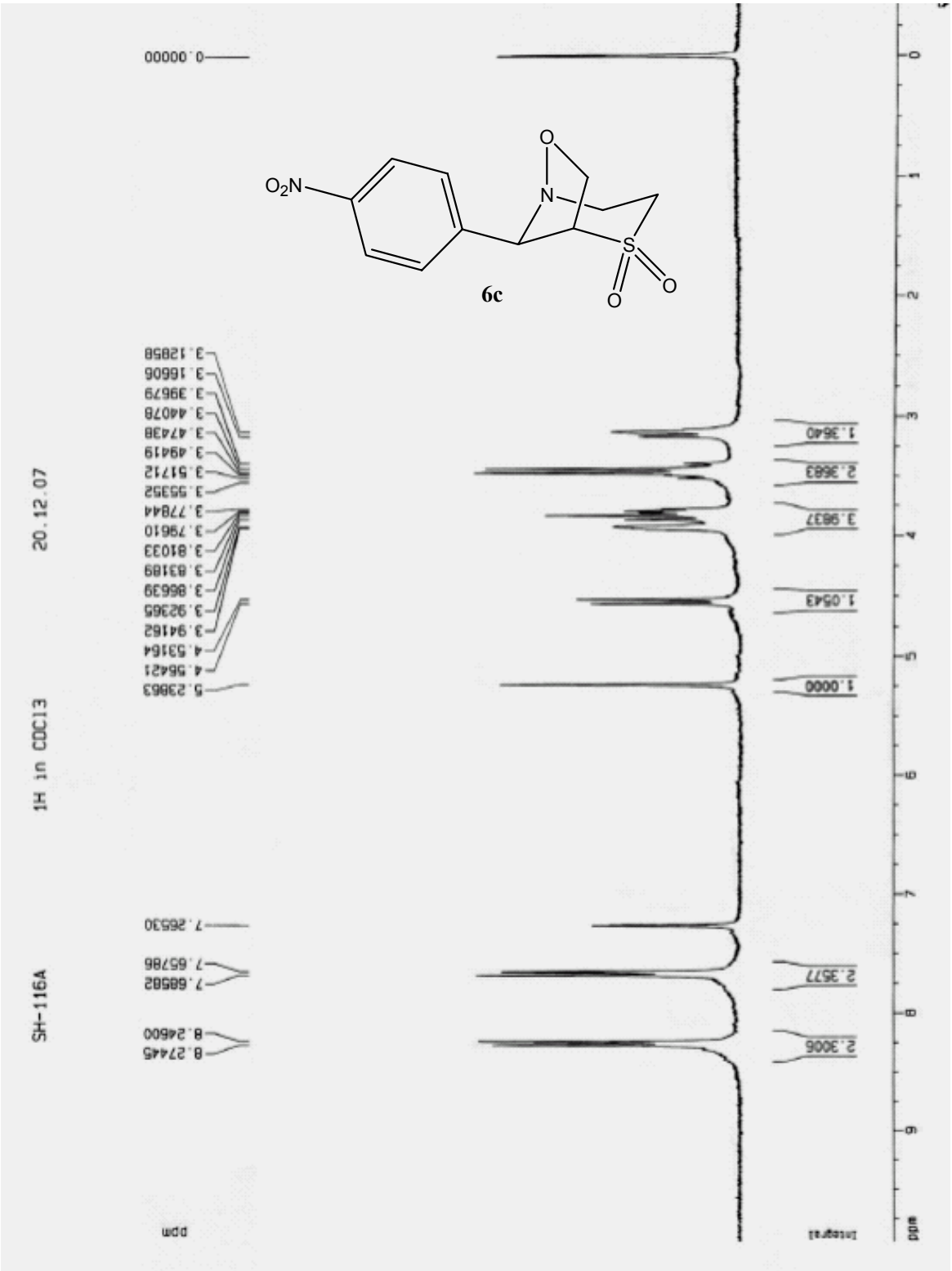
^{1}H NMR Spectrum of 6b:



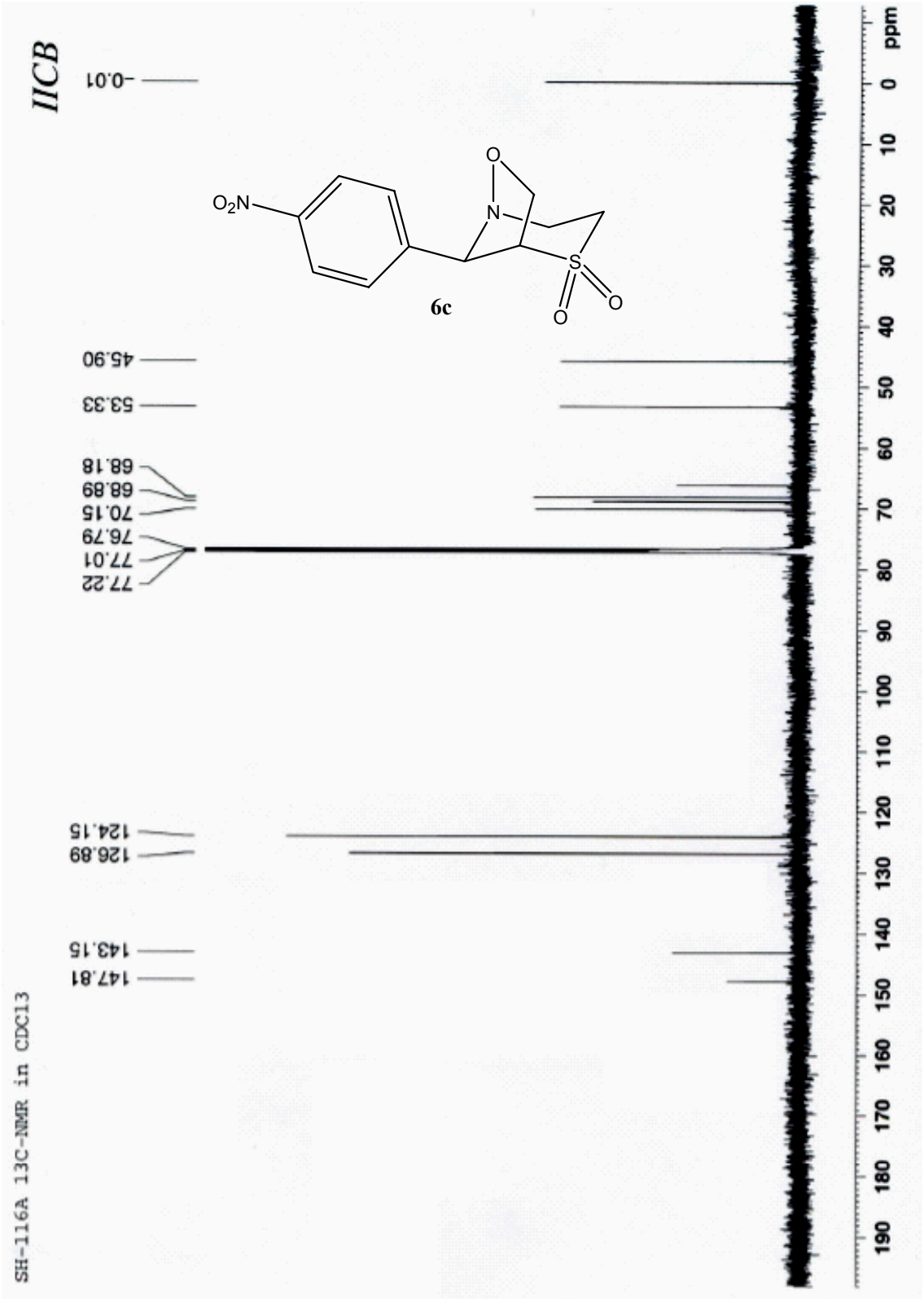
^{13}C NMR Spectrum of 6b:



^{1}H NMR Spectrum of 6c:

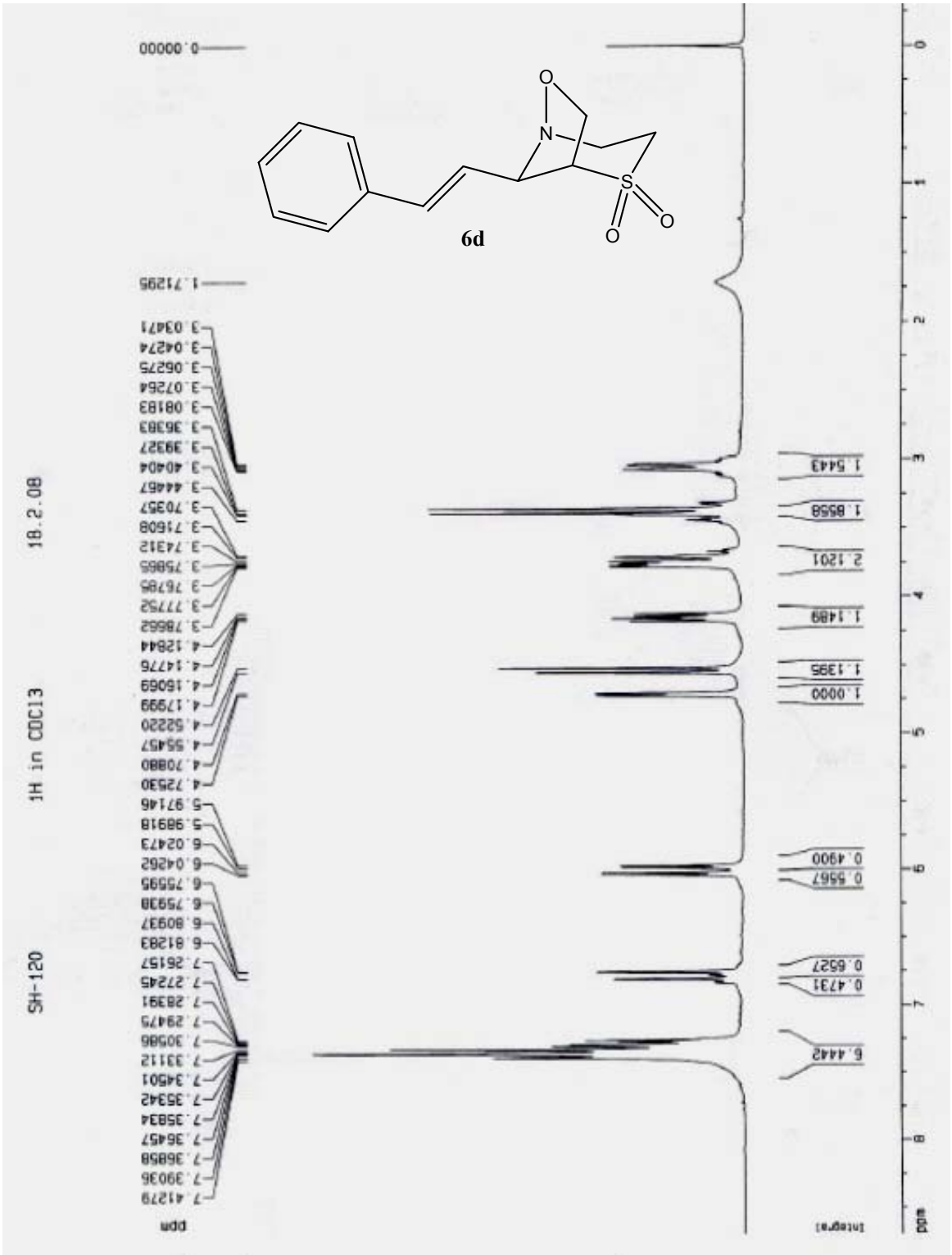


^{13}C NMR Spectrum of 6c:

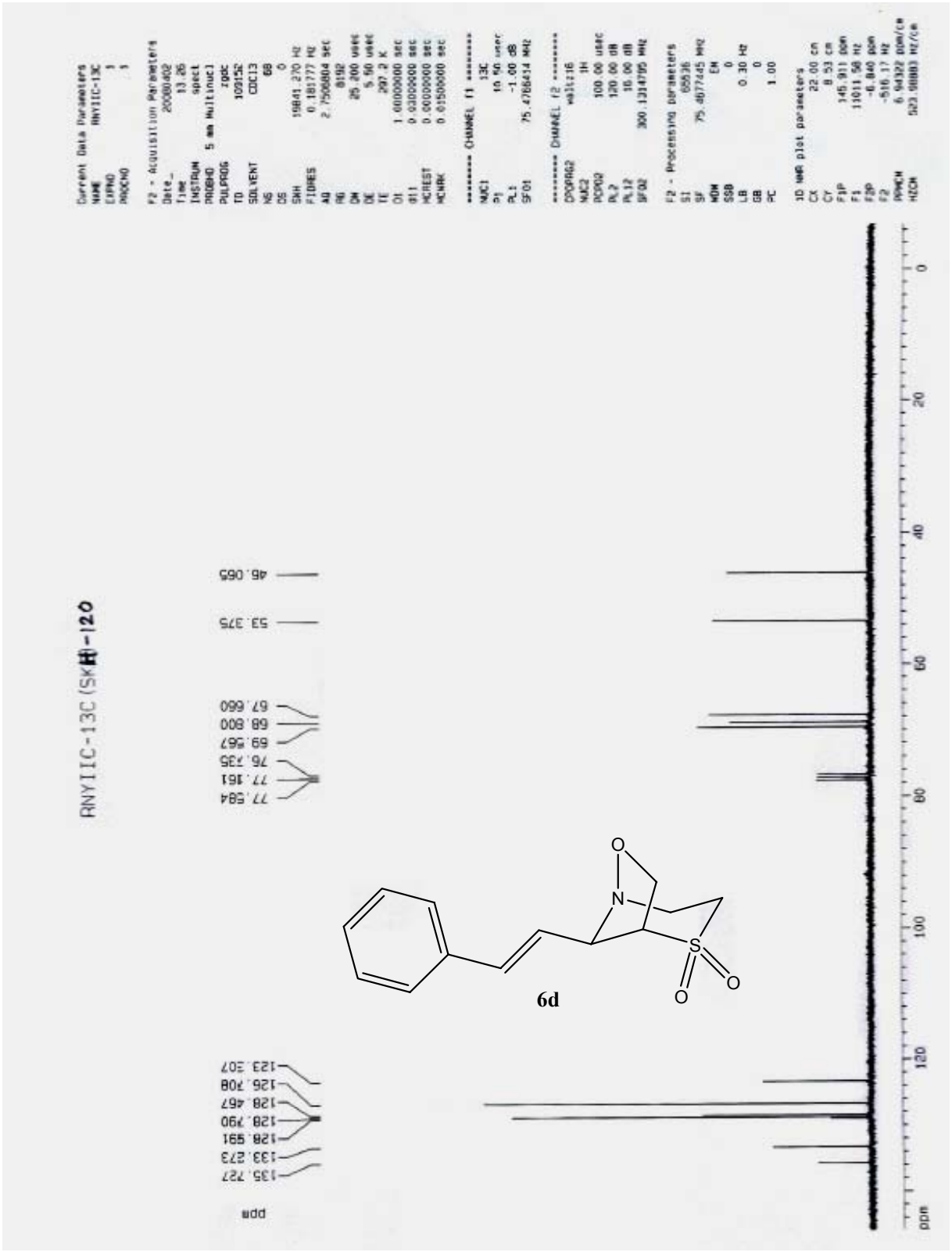


6c

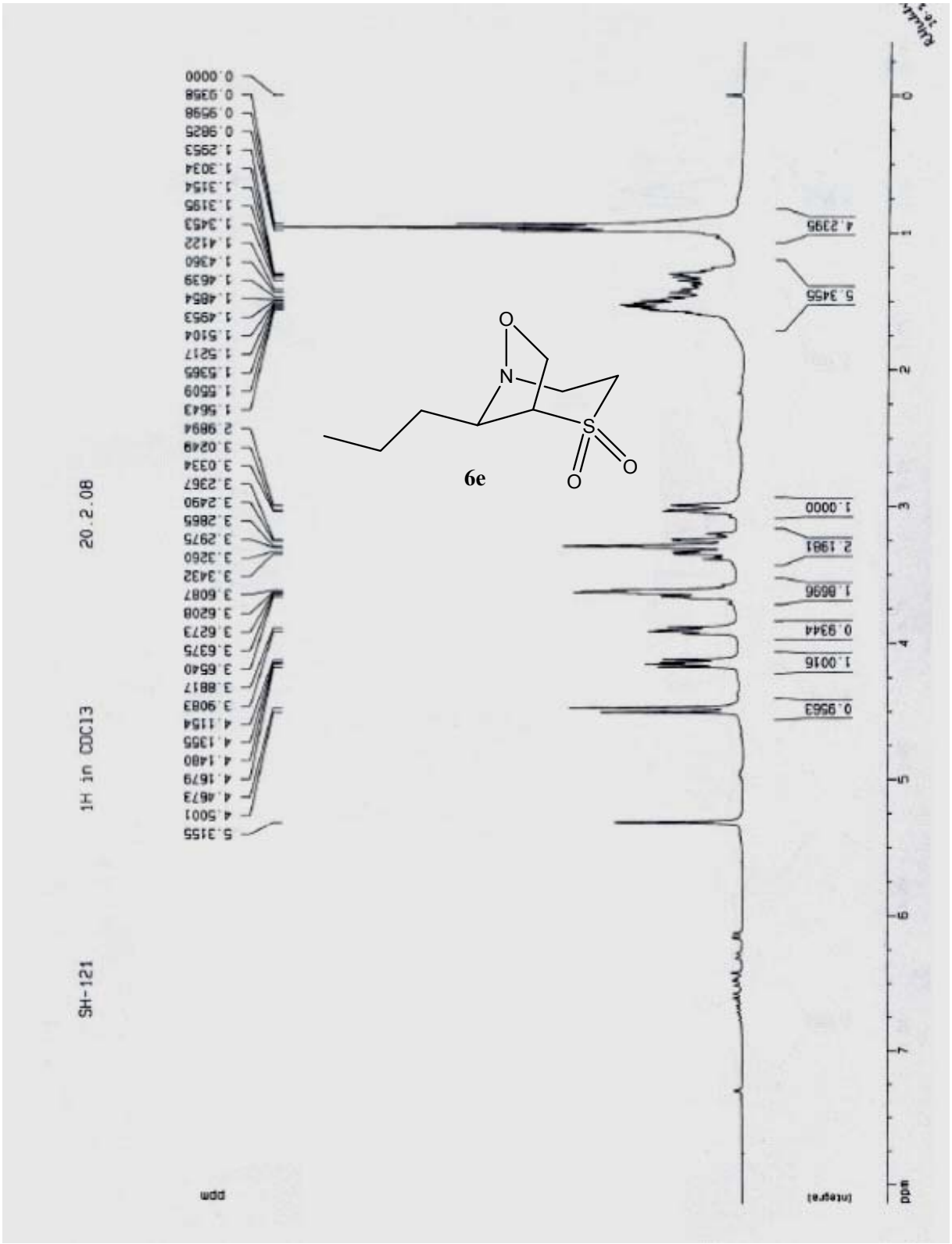
^{1}H NMR Spectrum of 6d:



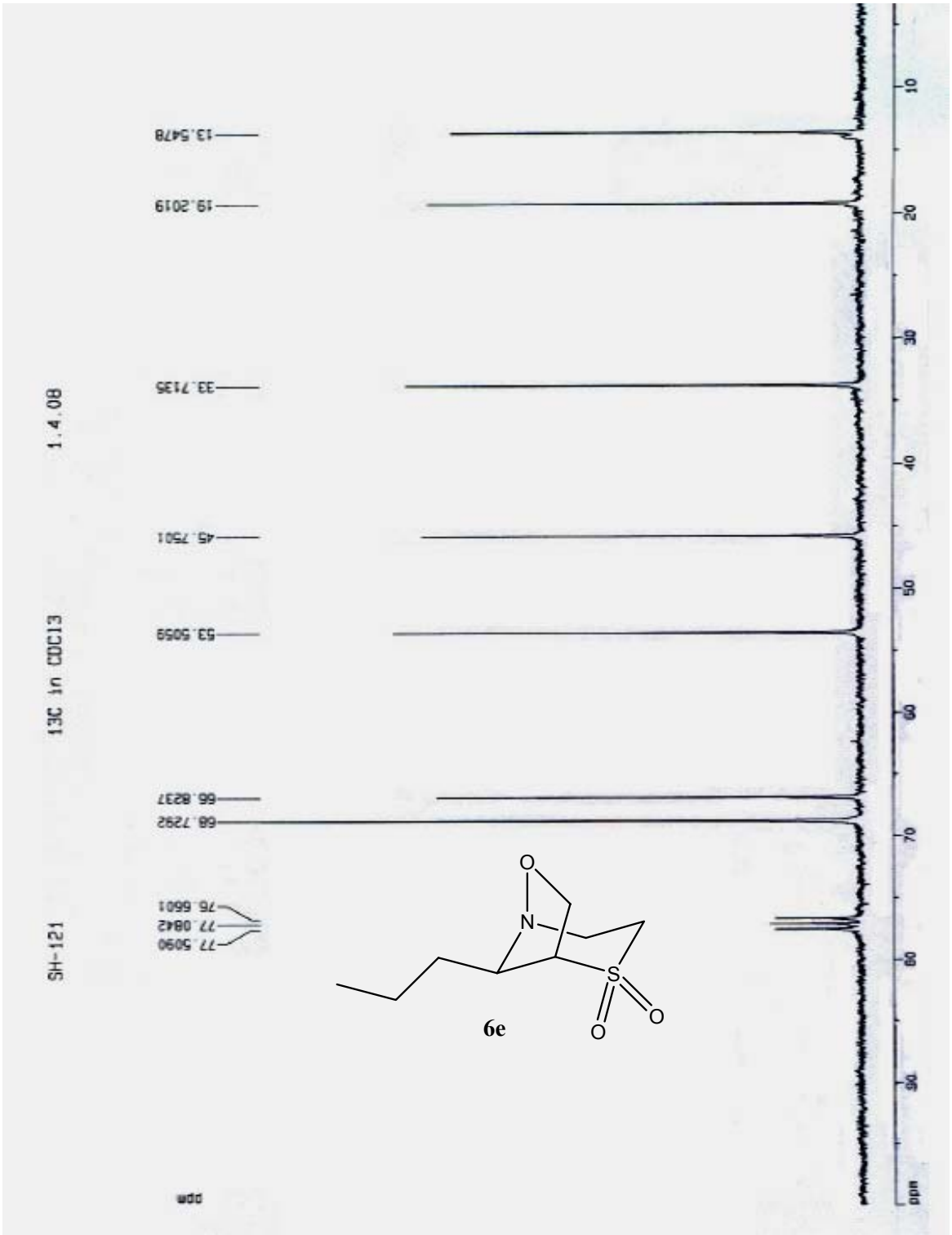
^{13}C NMR Spectrum of 6d:



^{1}H NMR Spectrum of 6e:



^{13}C NMR Spectrum of 6e:



6e