

**Supporting Information – Table of Contents**

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### 'Experimental Section'

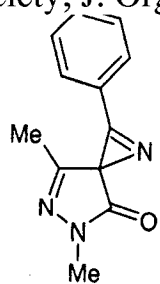
**General Methods.** Melting points were detected on a Kofler hot-stage microscope and are uncorrected. All NMR spectra were recorded on a 300 MHz spectrometer (300 MHz for  $^1\text{H}$ , 75 MHz for  $^{13}\text{C}$ ) at 28 °C. The center of the solvent signal was used as an internal standard which was related to TMS with  $\delta$  7.26 ppm ( $^1\text{H}$ ,  $\text{CDCl}_3$ ),  $\delta$  2.49 ppm ( $^1\text{H}$ ,  $\text{DMSO-}d_6$ )  $\delta$  77.0 ppm ( $^{13}\text{C}$ ,  $\text{CDCl}_3$ ), and  $\delta$  39.5 ppm ( $^{13}\text{C}$ ,  $\text{DMSO-}d_6$ ). Unambiguous assignment of signals and spin coupling constants was achieved on basis of standard 1D and 2D NMR techniques completed by such based on selective excitation such as 1D-TOCSY and 1D- as well as 2D long-range INEPT experiments. The numbering of atoms in the listings of NMR signals for compounds **2** is always given for the hydroxypyrazole form (A in Figure 1), for compounds **3** in the enaminyrazolone form (D in Scheme 1). With compounds **3**, not all lines of the corresponding minor isomers could be assigned unambiguously, owing to overlap with signals due to the predominating major isomer. Mass spectra (EI, 70 eV) were obtained on a Shimadzu QP 1000 spectrometer, IR spectra were measured on a Perkin Elmer FTIR 1605 spectrophotometer. CHN Analyses were carried out at the Microanalytical Laboratory, Department of Physical Chemistry, University of Vienna.

14/04/03 04:24 p.m.

C:\windows\Escritorio\Holzer-2\spectra.zip

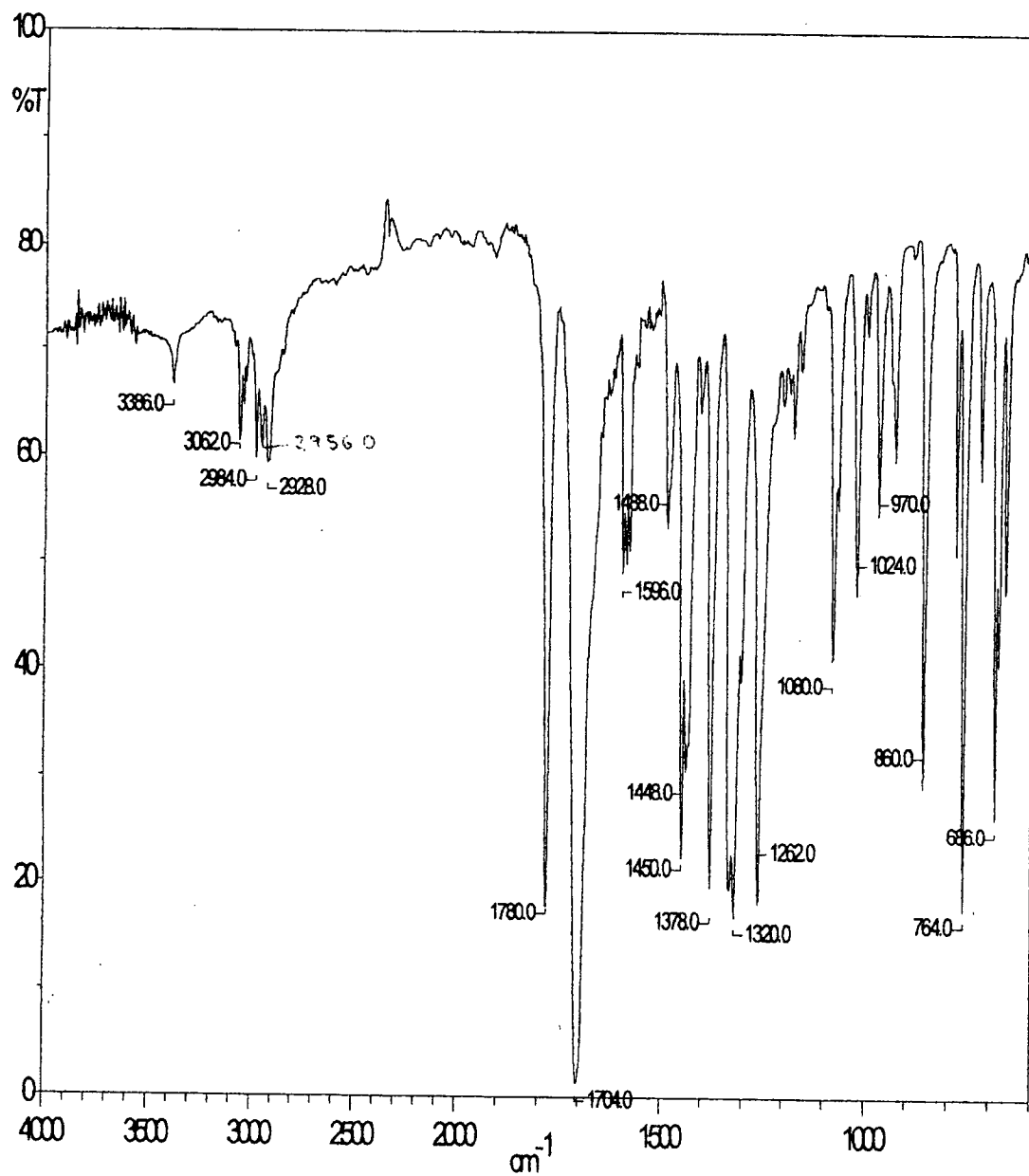
Page 1

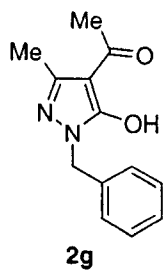
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4a

IR (KBr)





<sup>1</sup>H NMR (CDCl<sub>3</sub>)

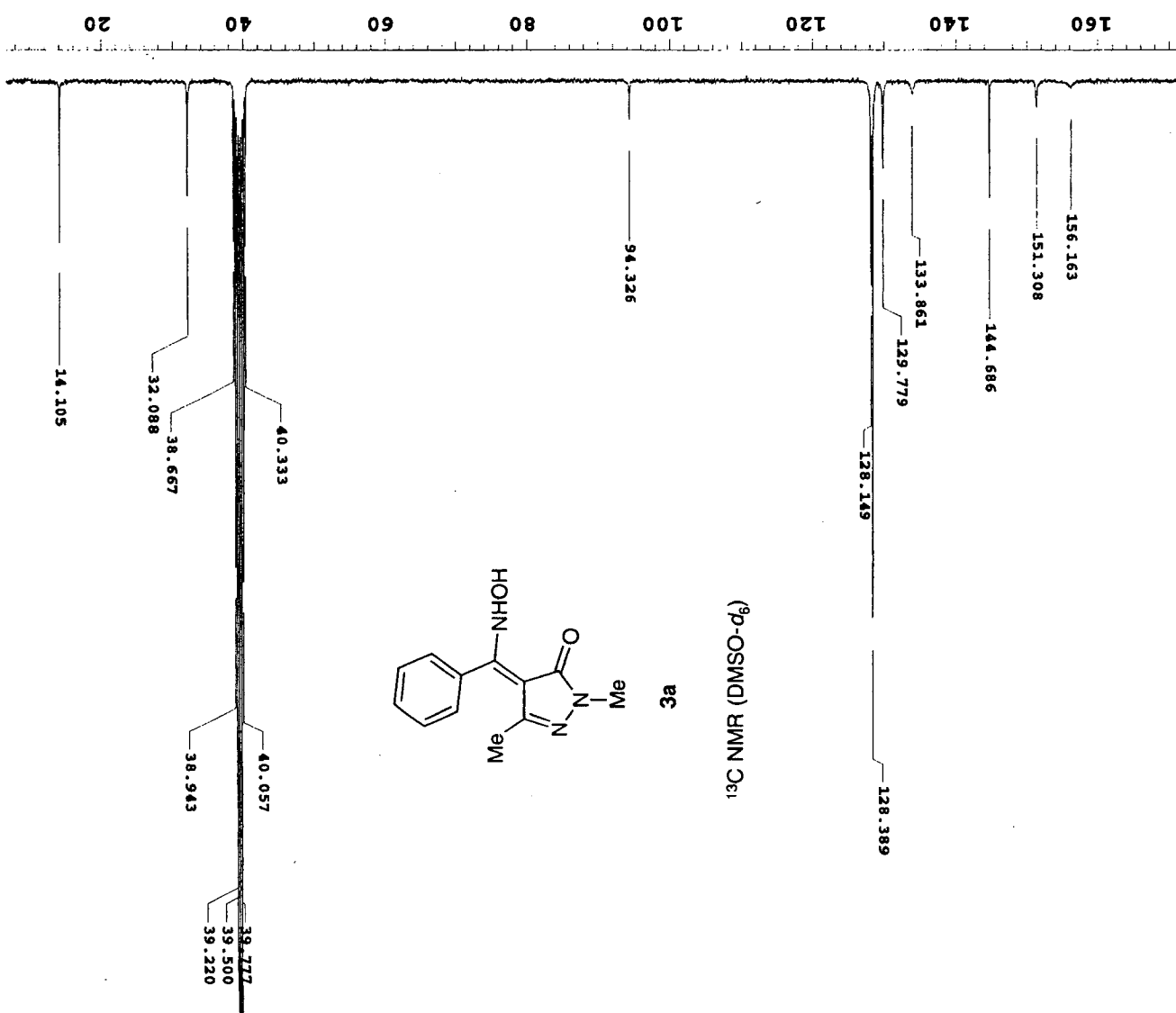
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fb 2200
bs 4
tpwr 57
pw 7.0
dl 5.000
tof 600.0
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ct 16
alock n
gain 44
il n
cp n
hs n
SP 299.9
WP 2699.4
VS 100
SC 0
WC 200
hzmm 13.50
is 134.77
xf1 2510.7
zfp 2177.5
th 4.804
em ph
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dmn C
dmc 200
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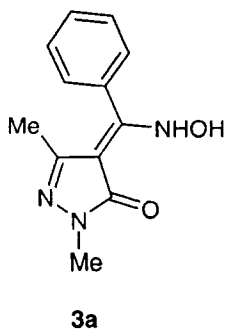
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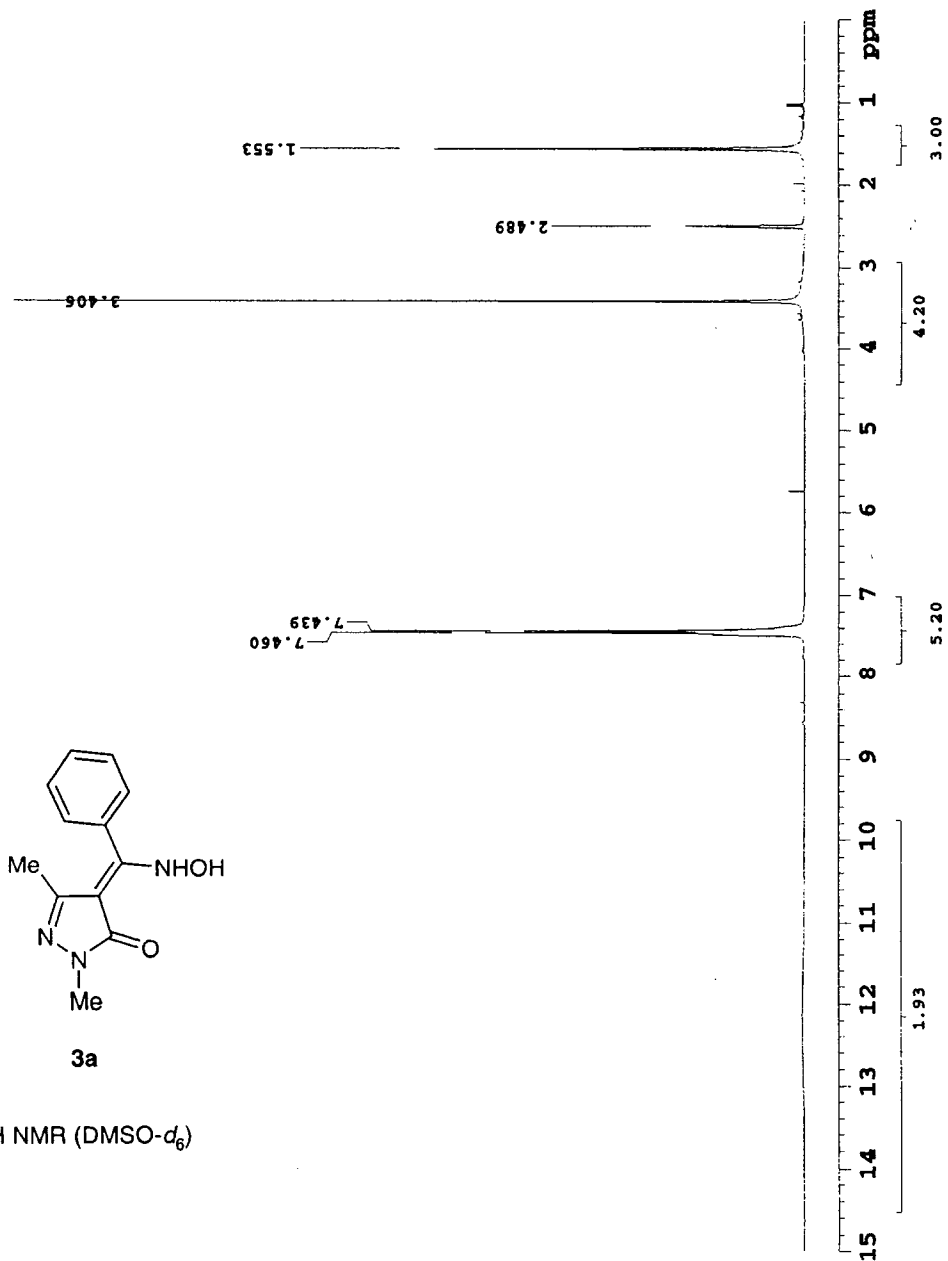
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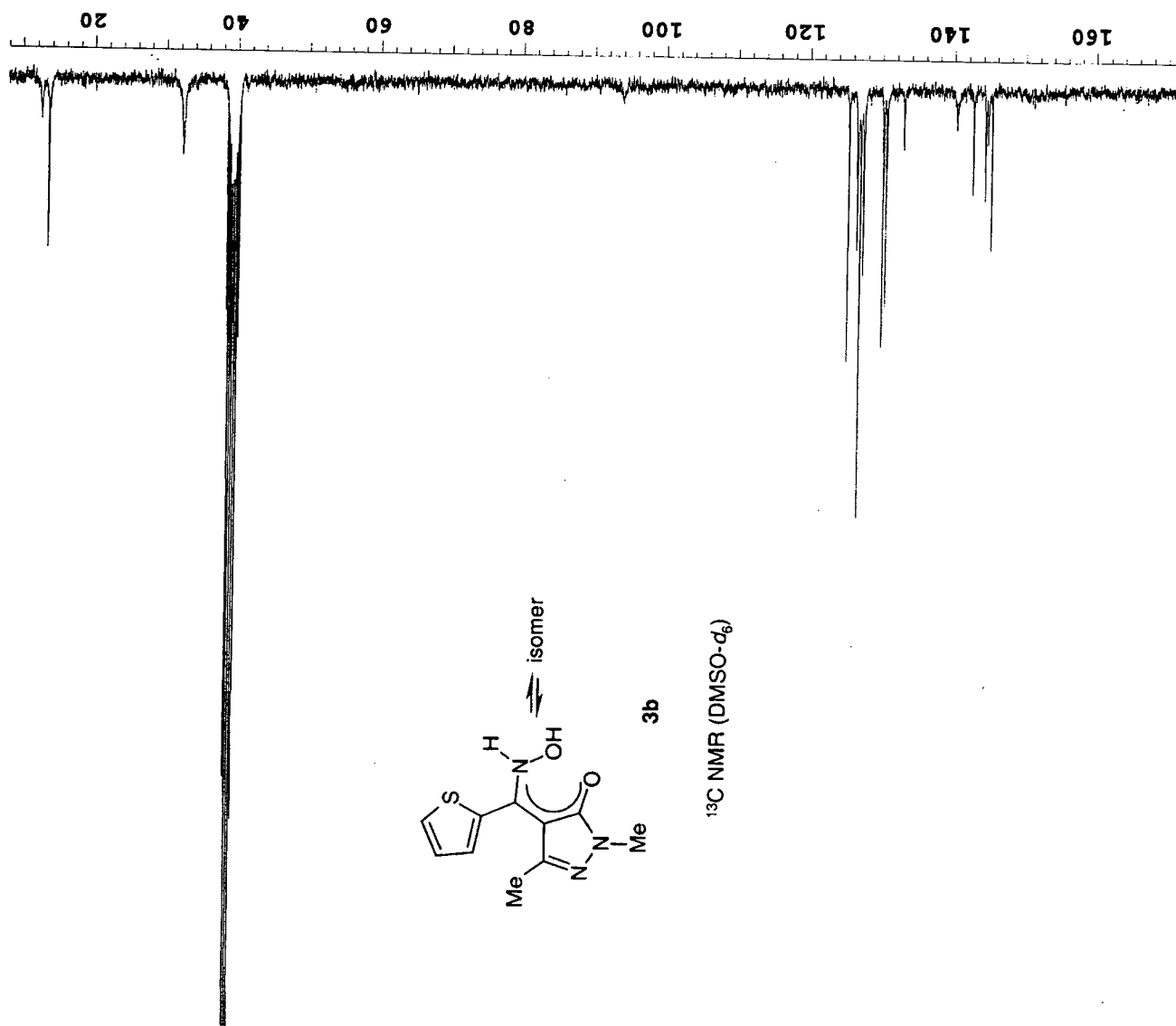
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VC 0
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XIP 746.9
CH 15
INS 3.615
nm ph
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gf not used
sfs not used
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y whs
nn wnt
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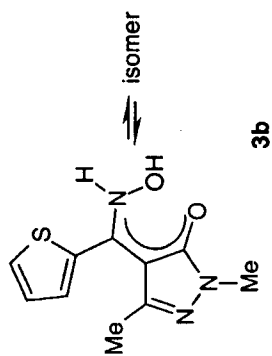
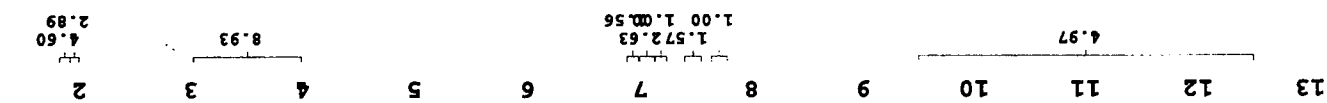


<sup>1</sup>H NMR (DMSO-d<sub>6</sub>)

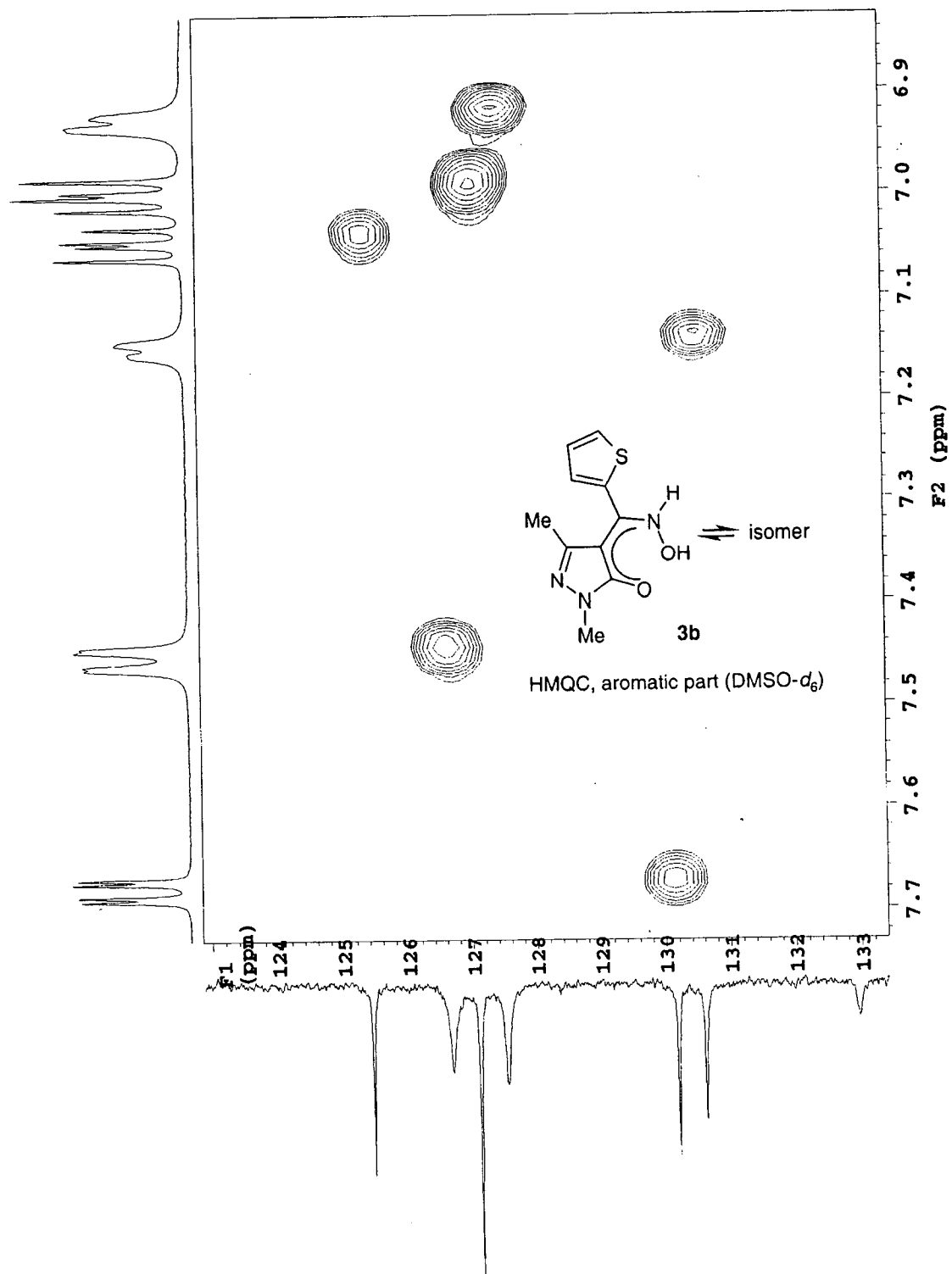


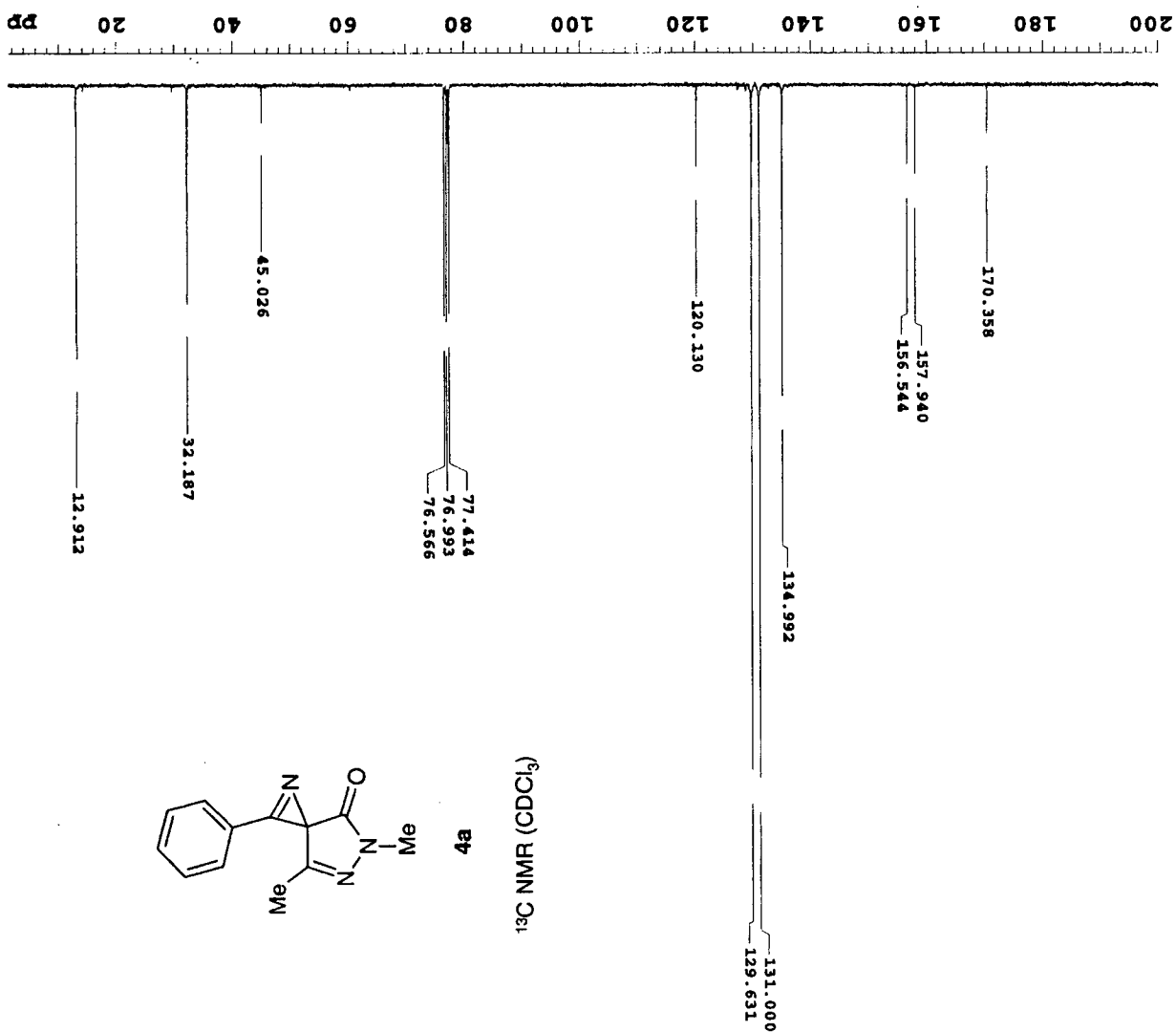


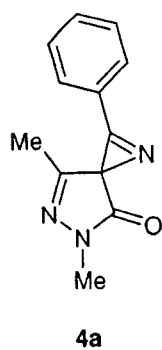




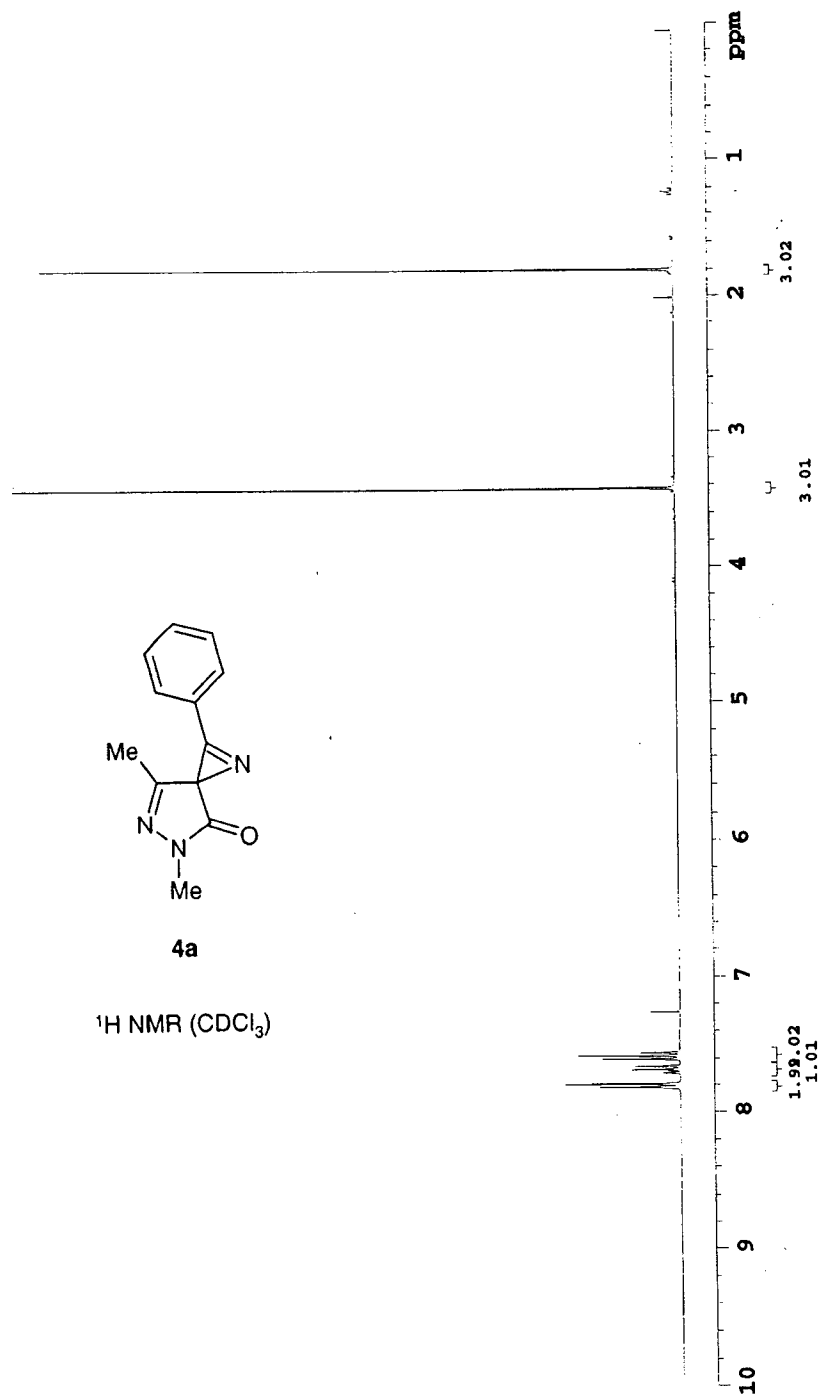
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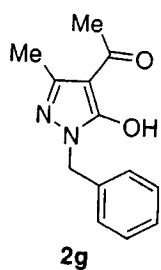




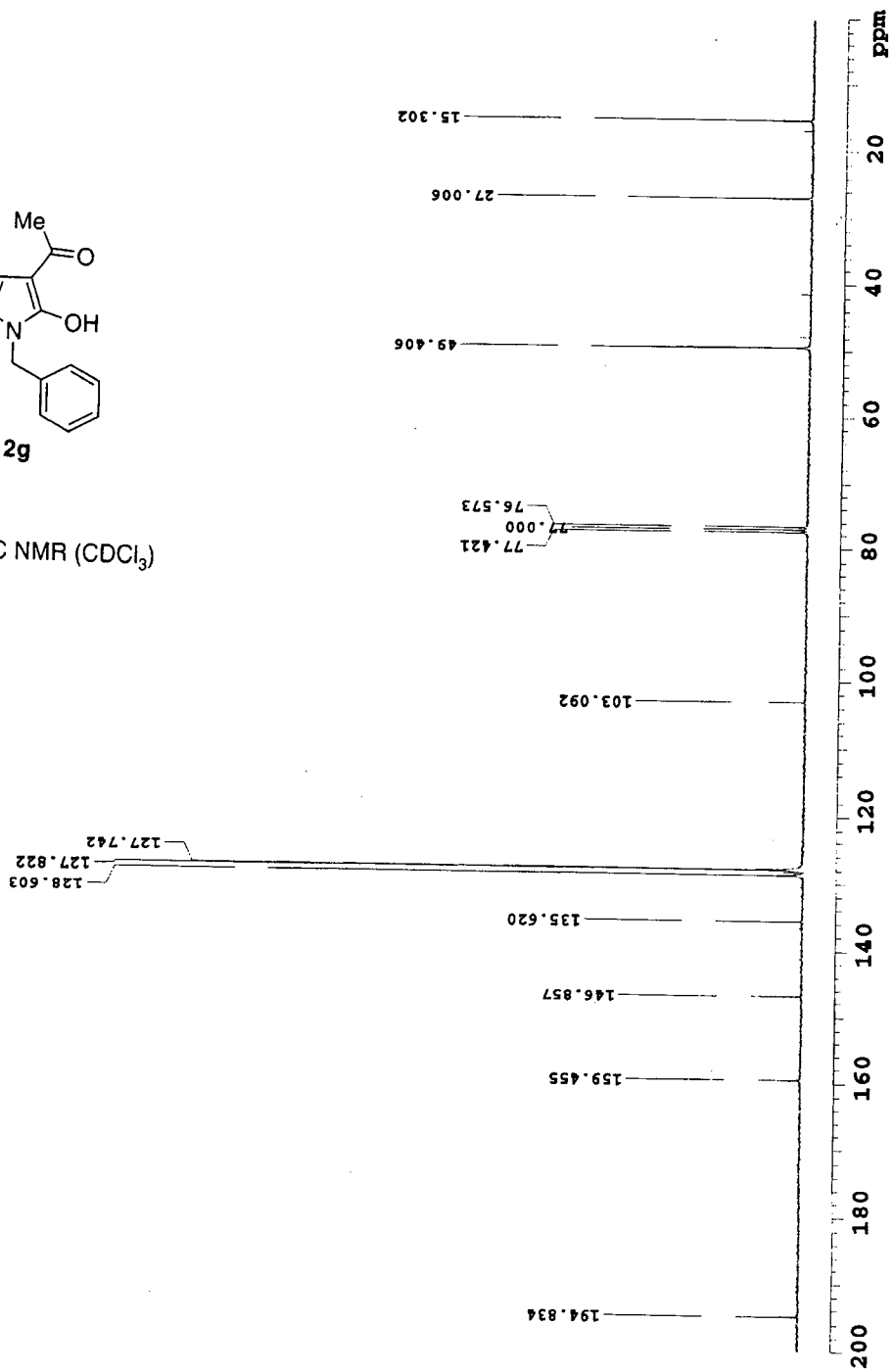


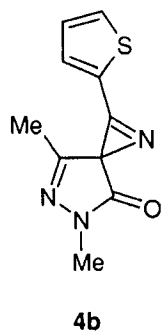
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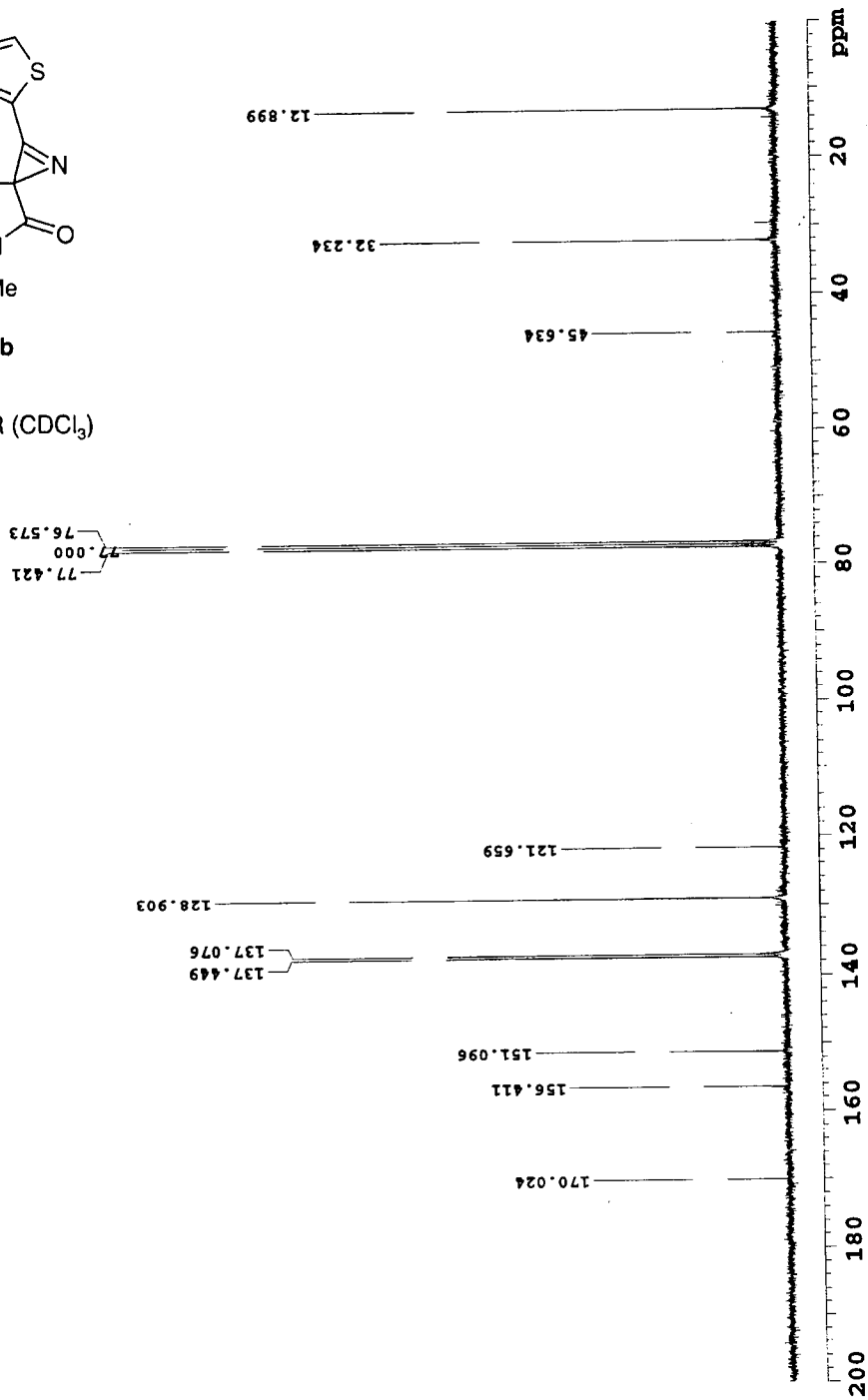


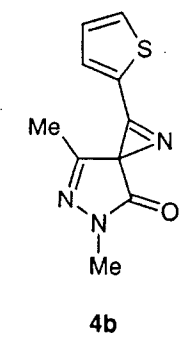
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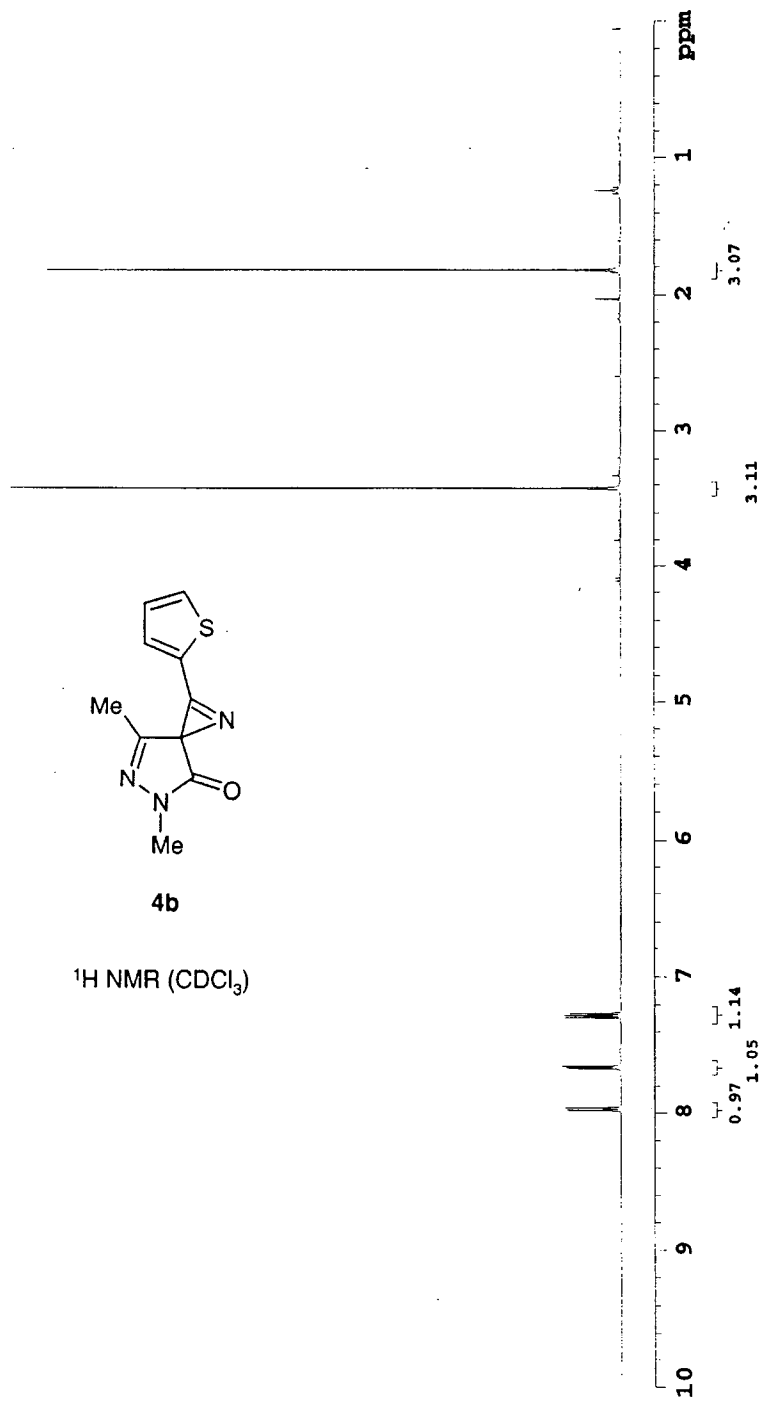


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )





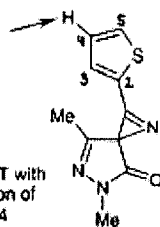
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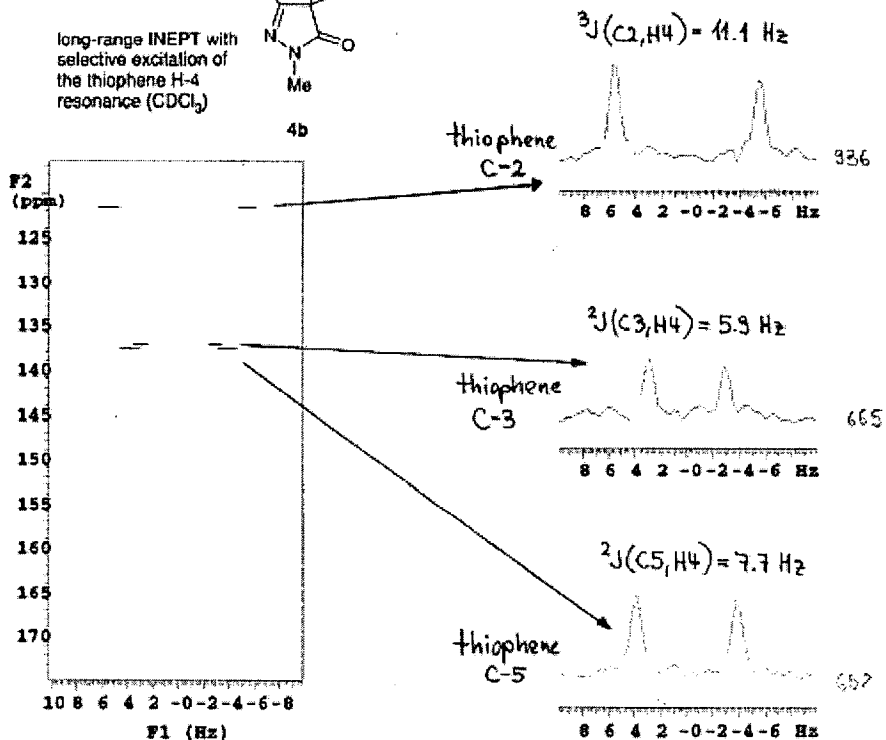
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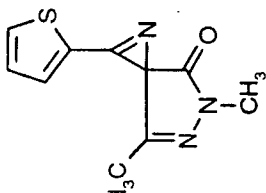
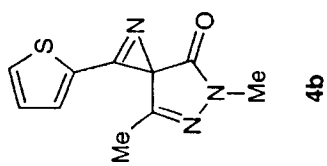
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long-range INEPT with selective excitation of the thiophene H-4 resonance (CDCl<sub>3</sub>)

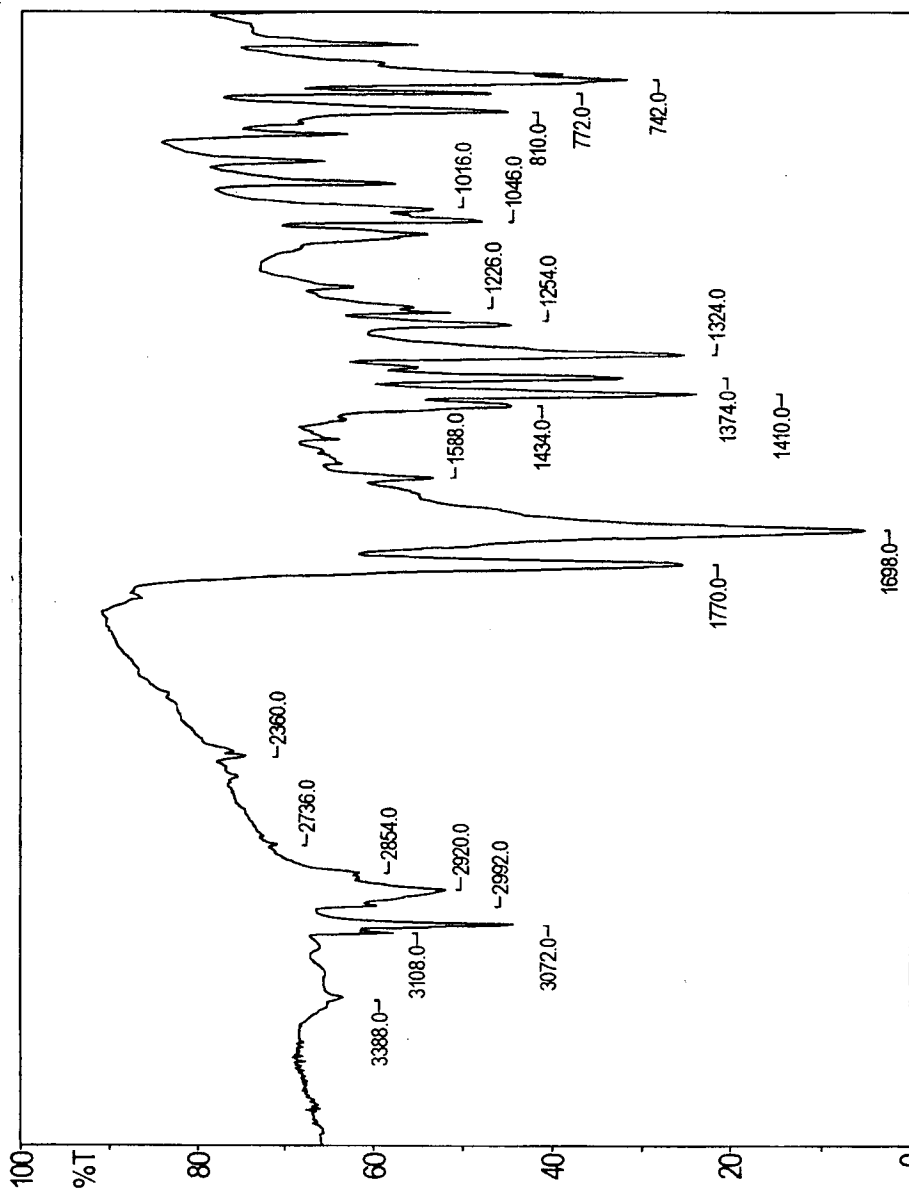


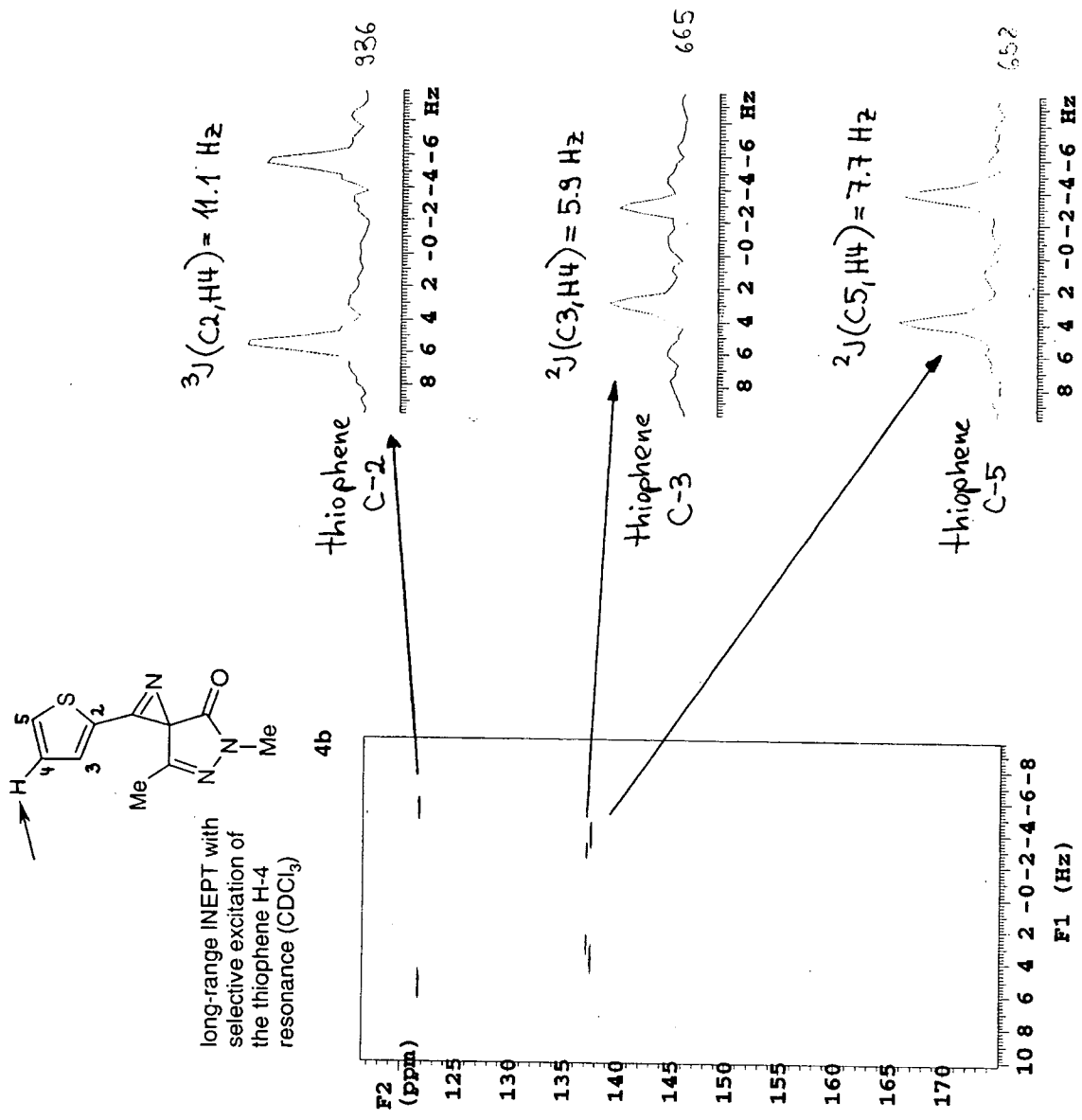




IR (KBr)

(MG=219,27)





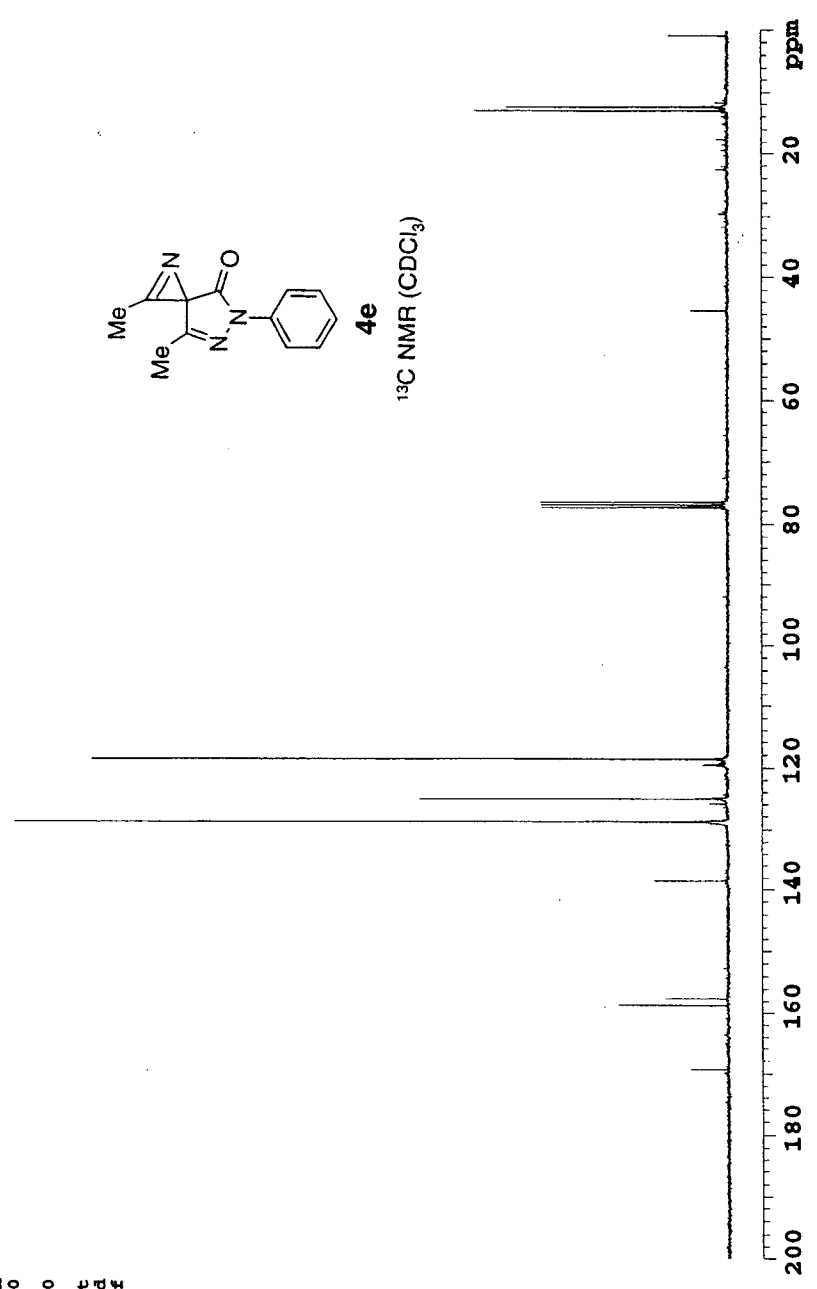
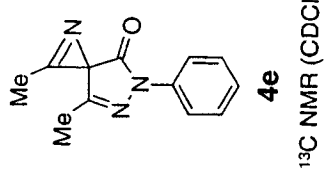
(H-4)

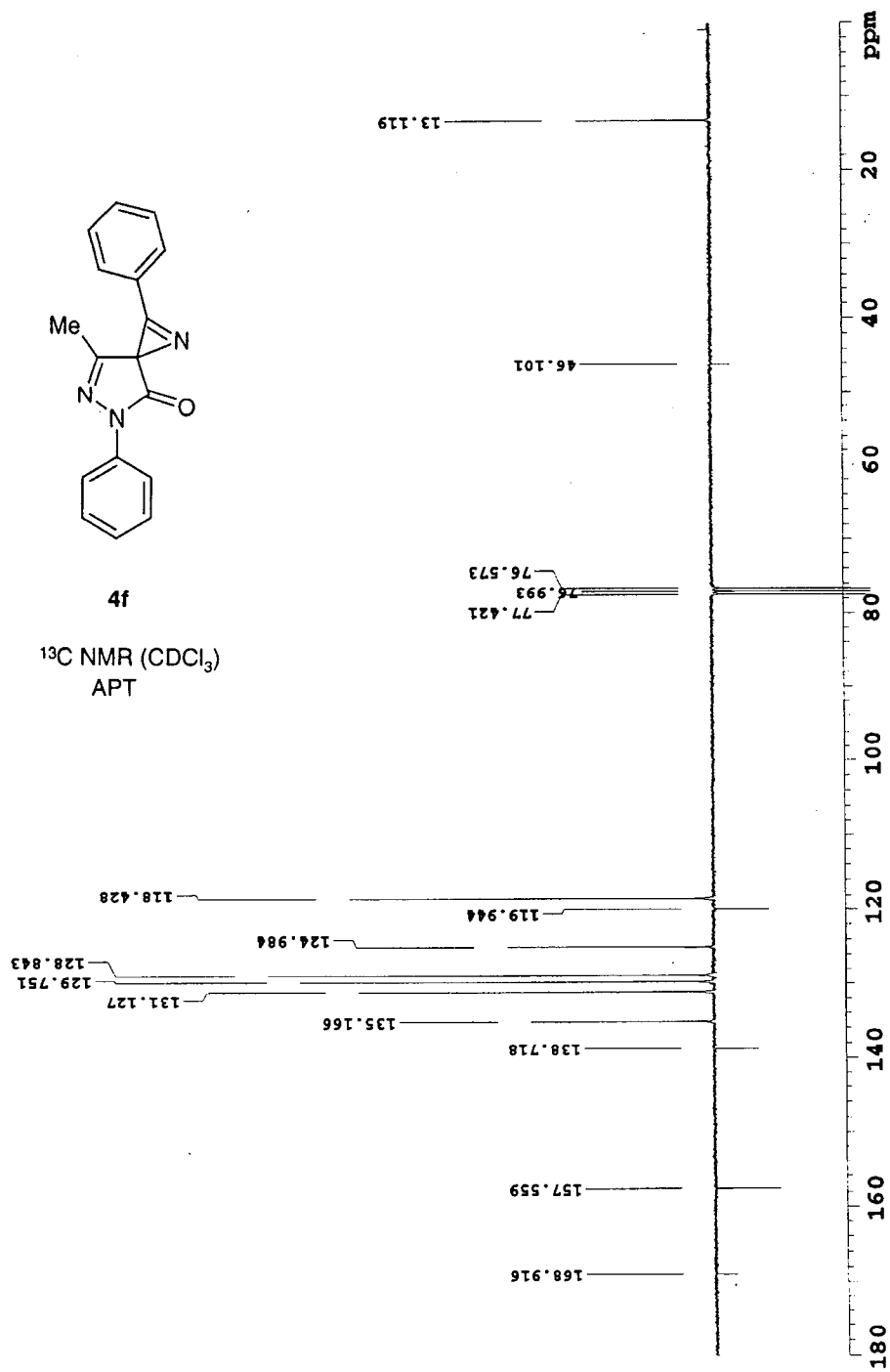
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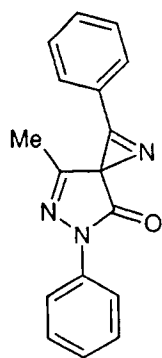
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tof 3565.7 wexp
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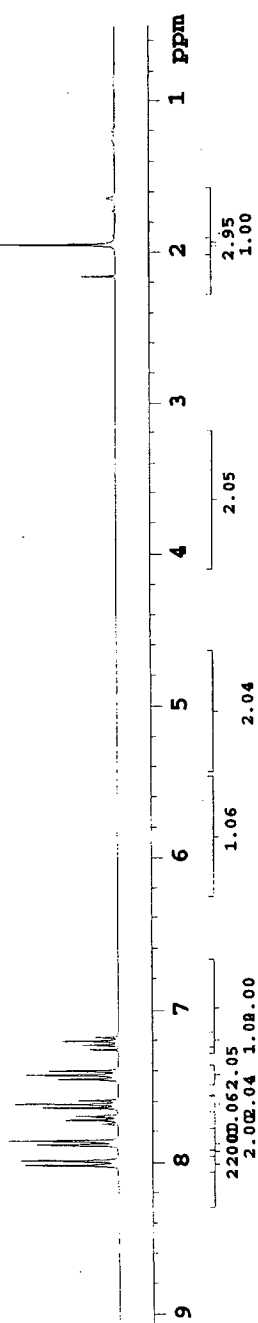


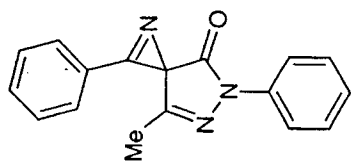




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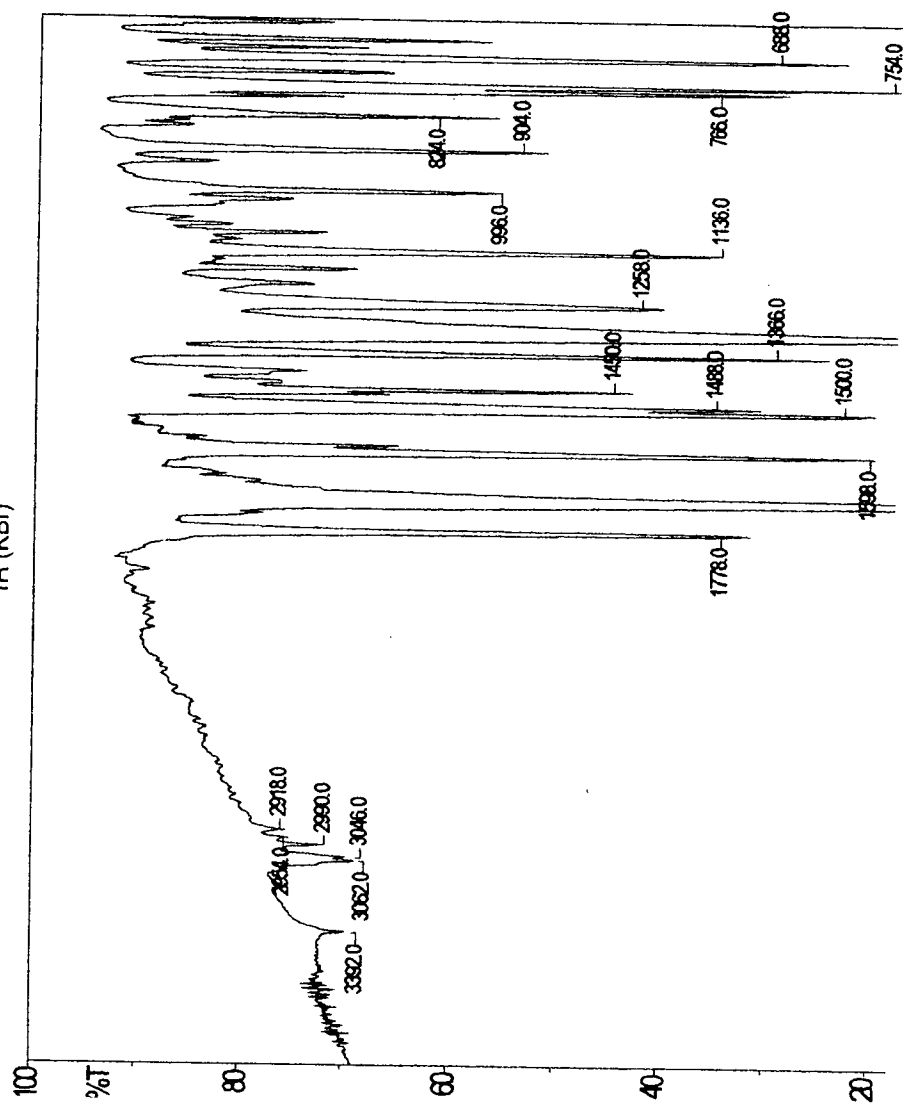
<sup>1</sup>H NMR (CDCl<sub>3</sub>)





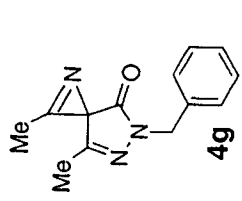
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IR (KBr)

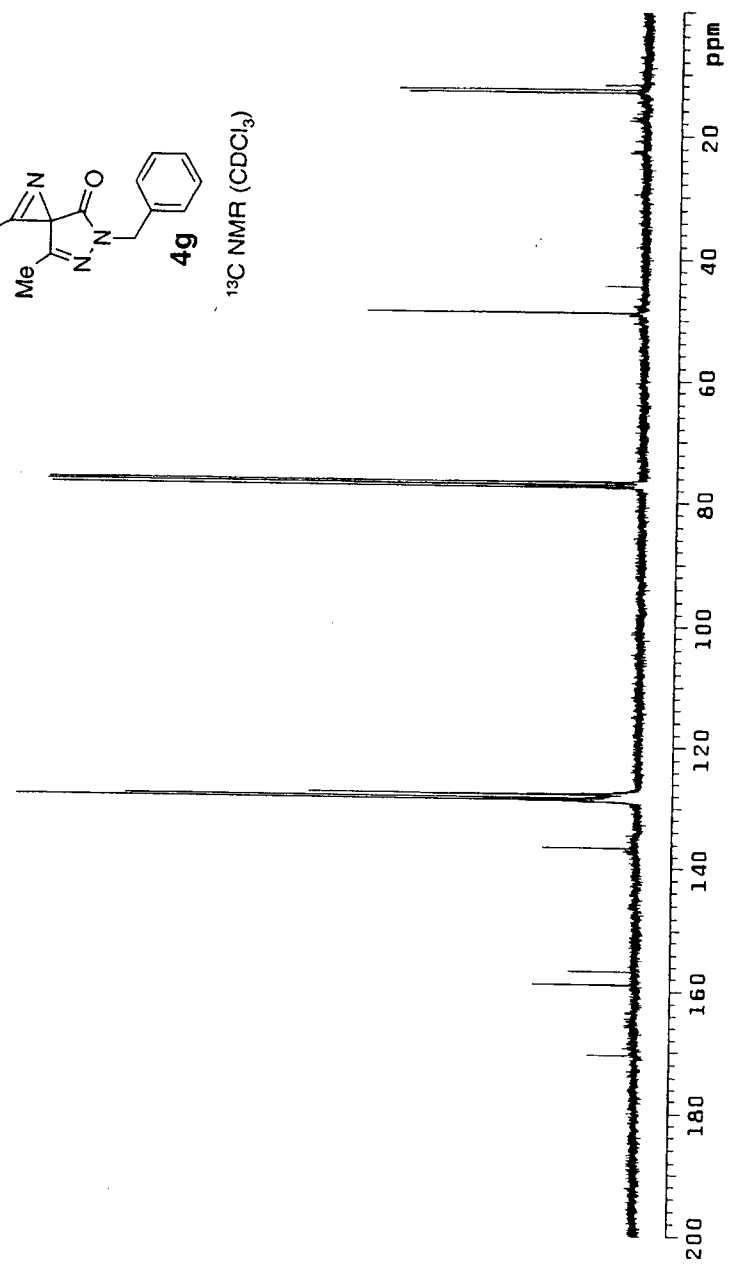


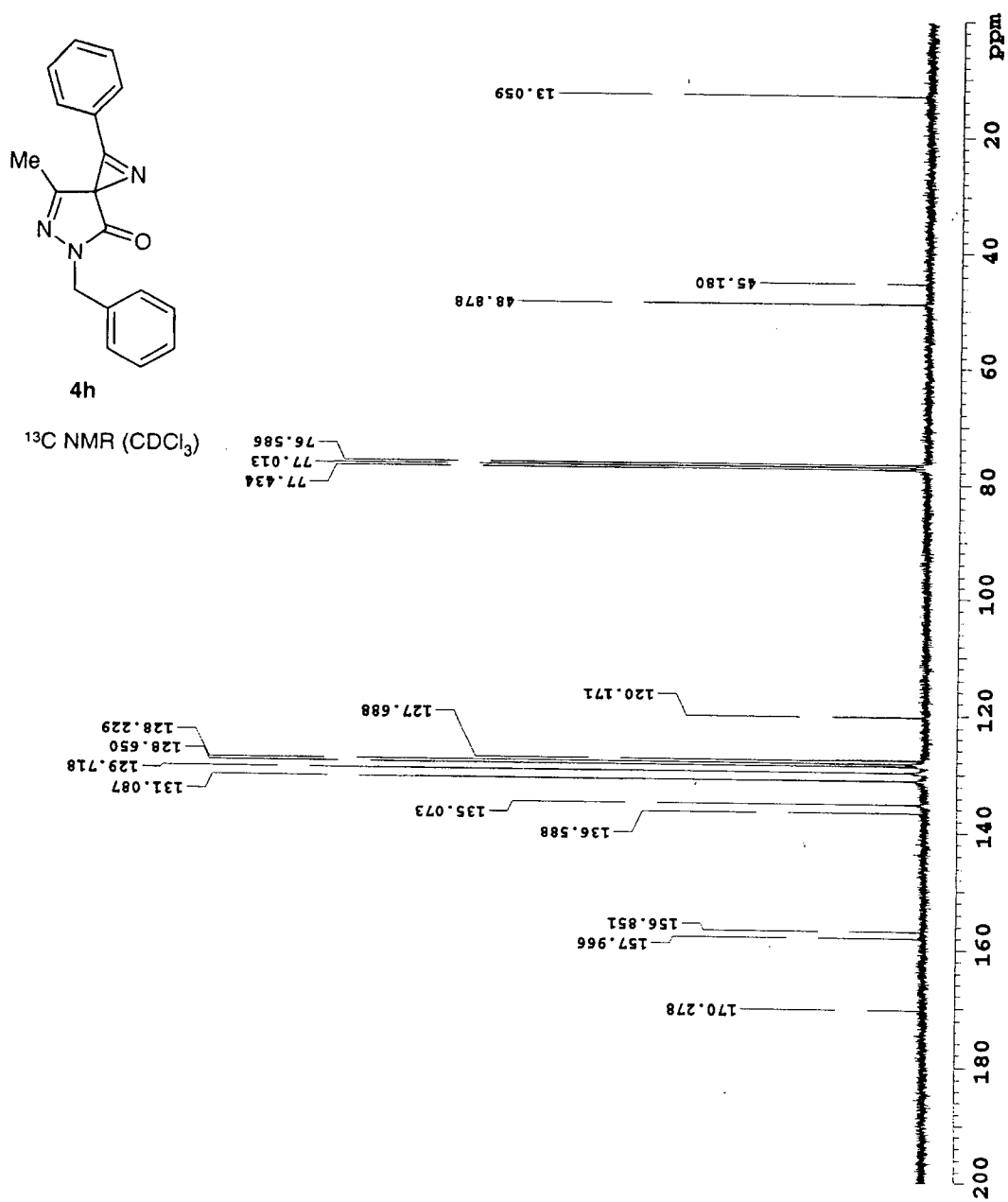
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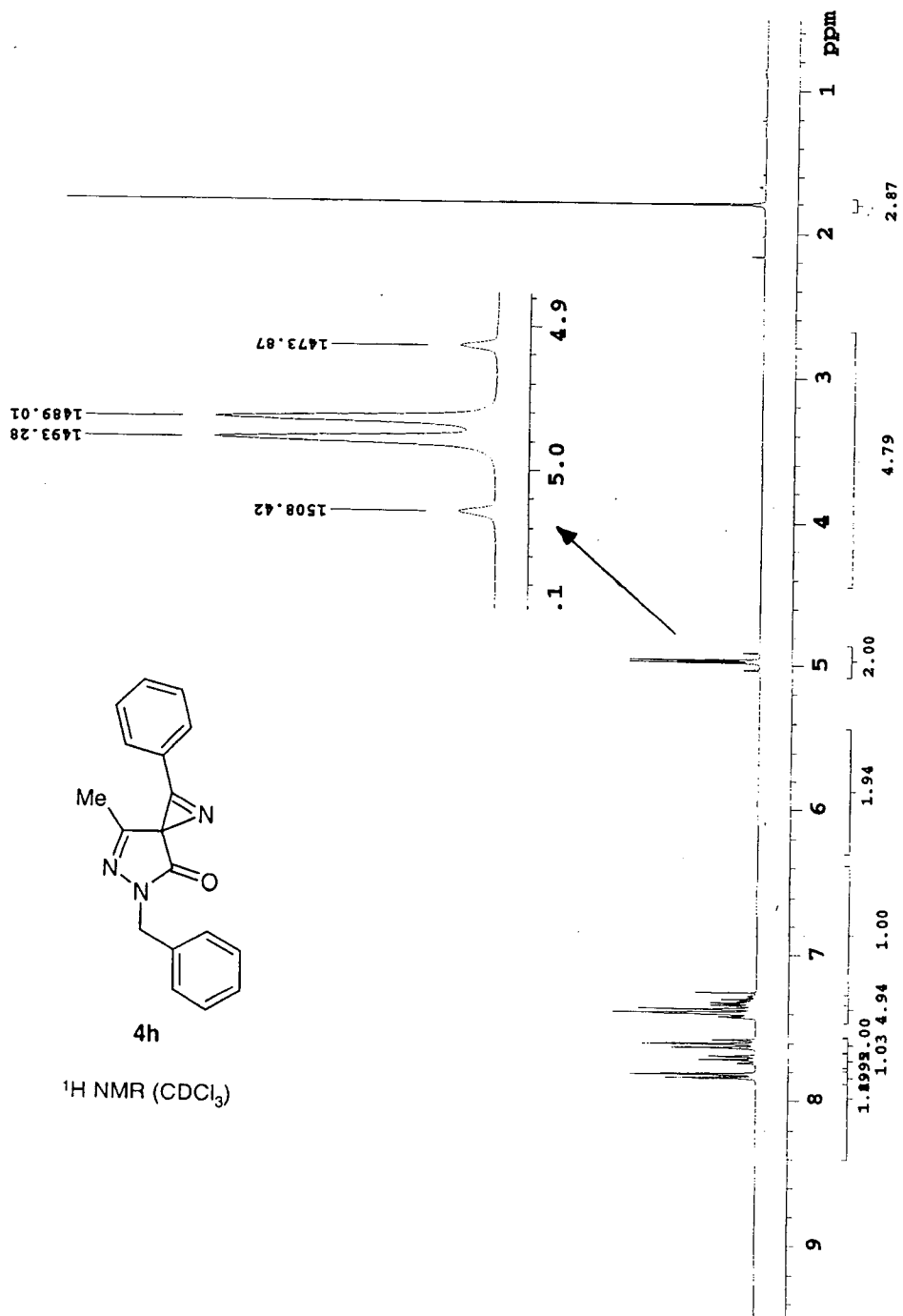


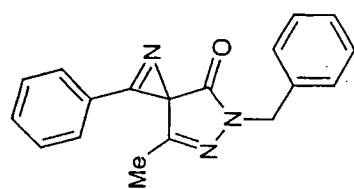
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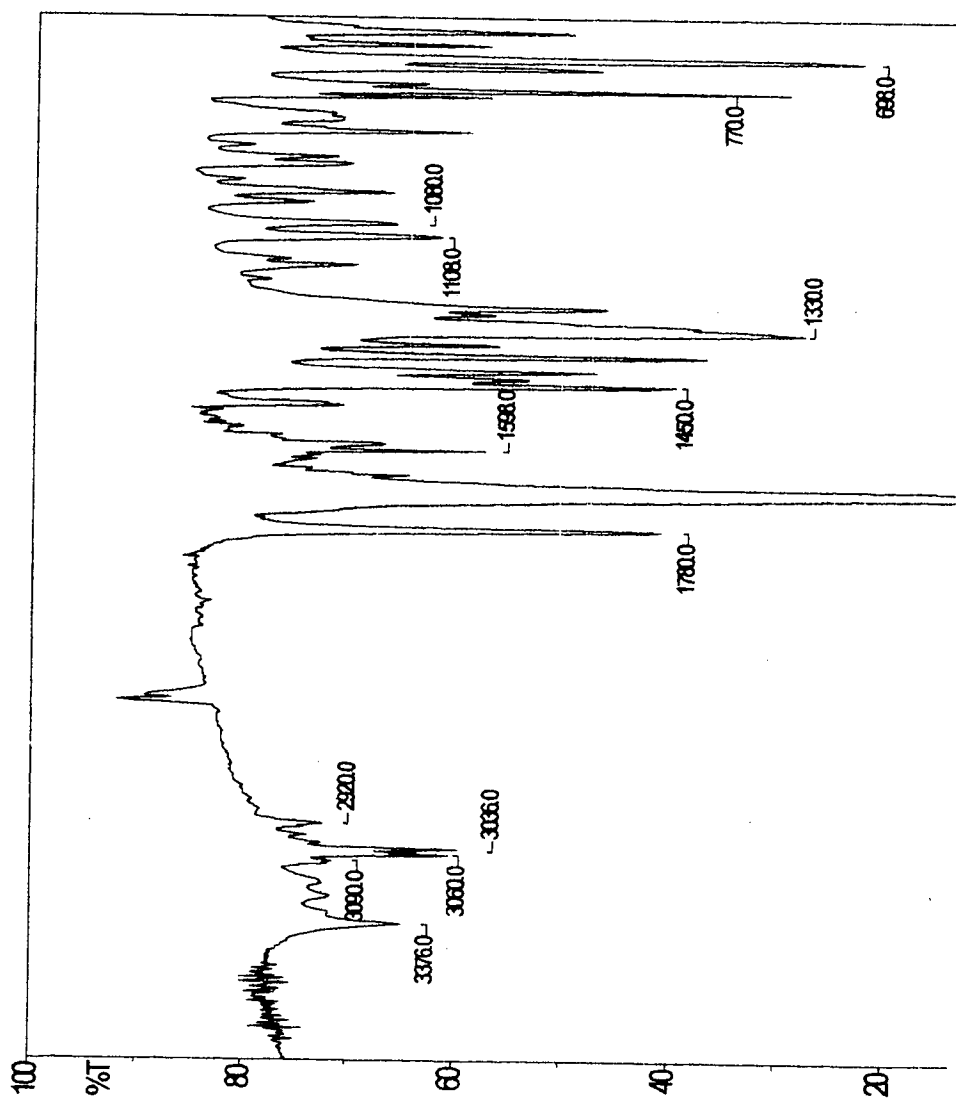




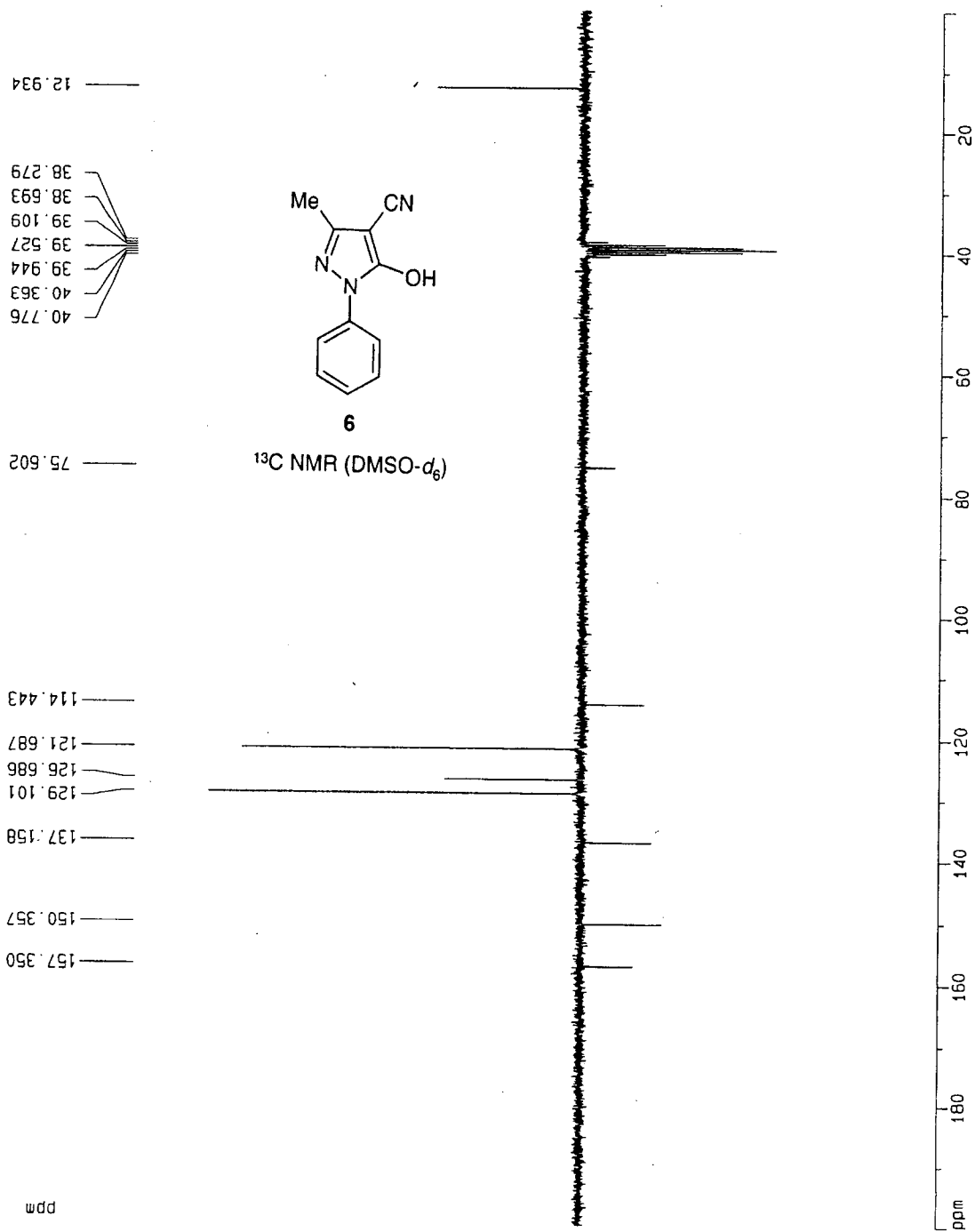




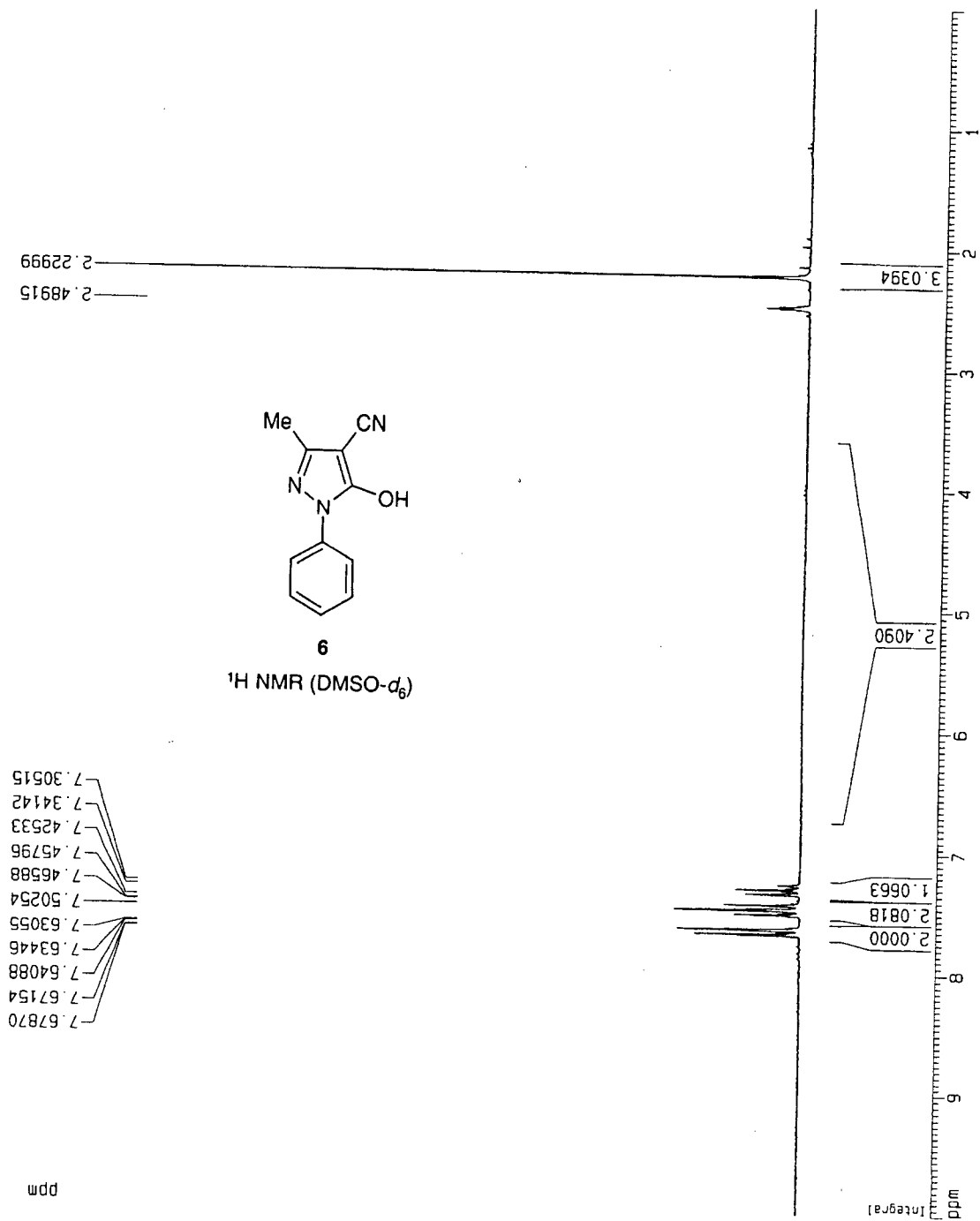
4h  
IR (KBr)

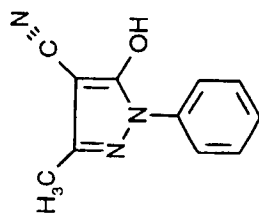
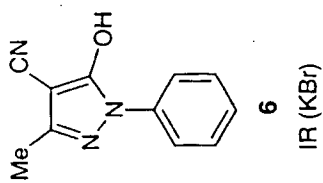


06 S27/saure Phase/DMSO



DG S27/saure Phase / DMSO





(MG=199,21)

