

9-2-99

1

A New Reaction of 2-(Phenylsulfonyl)-3-phenyloxaziridine (Davis Reagent): Oxidation of Thiolates to Sulfinates. Application to the Synthesis of Sulfones

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Supporting Information

Typical Procedure with the Synthesis of Sulfone 6a₃: To a cooled (-78 °C) solution of thiophenol **5a** (110 mg, 1 mmol) in THF (1.5 ml) was added dropwise MeLi (0.69 ml of a 1.6 N solution in Et₂O, 1.1 mmol). After stirring the solution at -78 °C for 15 min, a solution of oxaziridine **1** (548 mg, 2.1 mmol) in THF (1.2 ml) was added dropwise very slowly (exothermic reaction). The reaction mixture was warmed to -40 °C (15 min) and around this temperature the mixture became cloudy. The solution was then stirred at -10 °C (ice/NaCl bath) for 15 min and AcOEt (30 ml) was added. The sulfinate salt was extracted with pure H₂O (3 × 3 ml). The combined aqueous extracts were washed with AcOEt (4 × 30 ml), concentrated, and dried overnight under high vacuum to provide quantitatively the pure sulfinate salt.*

A mixture of the above sulfinate salt, tetrabutylammonium bromide (25 mg) and allyl bromide (181 mg, 1.5 mmol) was heated to 80-85 °C for 24 h in a solvent system consisting of toluene (0.3 ml), acetone (0.3 ml) and water (0.4 ml). After cooling to room temperature, the reaction mixture was poured into a saturated aqueous NaCl solution (2 ml) and the product was extracted with Et₂O (3 × 30 ml). The combined organic extracts were dried over MgSO₄, filtered, and concentrated. The resulting crude product was purified by column chromatography (light petroleum ether/ethyl acetate, 80:20) to afford sulfone **6a₃** (167 mg, 0.91 mmol, 91%) as a colorless oil.

* The weight of the sulfinate salt was slightly superior, due probably to remaining water.

1-Methyl-2-ethylsulfanyl-4-(1,1-dimethylethyl)benzene 3: HRMS: calcd for C₁₃H₂₀S (M⁺) 208.1285, found 208.1281.

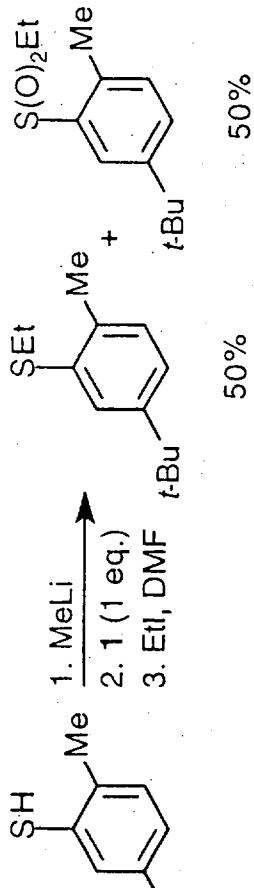
1-Methyl-2-ethylsulfonyl-4-(1,1-dimethylethyl)benzene 4: Anal. Calcd for C₁₃H₂₀O₂S: C, 64.97; H, 8.59; S, 13.32. Found: C, 64.98; H, 8.39; S, 13.26.

1-Ethylsulfanyl-4-methylsulfonylbenzene 6f: mp 88 °C (recrystallized from Et₂O); Anal. Calcd for C₉H₁₂O₂S₂: C, 49.97; H, 5.59; O, 14.79; S, 29.64. Found: C, 49.81; H, 5.61; O, 14.93; S, 29.46.

1-Ethylsulfinyl-4-methylsulfinylbenzene 8: mp 87-89 °C (recrystallized from AcOEt-pentane); HRMS: calcd for C₉H₁₂O₂S₂ (M⁺) 216.0279, found 210.0278.

Conditions for NMR spectra:

¹H NMR: 250 MHz, CDCl₃, TMS and ¹³C NMR: 62.5 MHz, CDCl₃, TMS



¹H NMR (CDCl₃)

of product

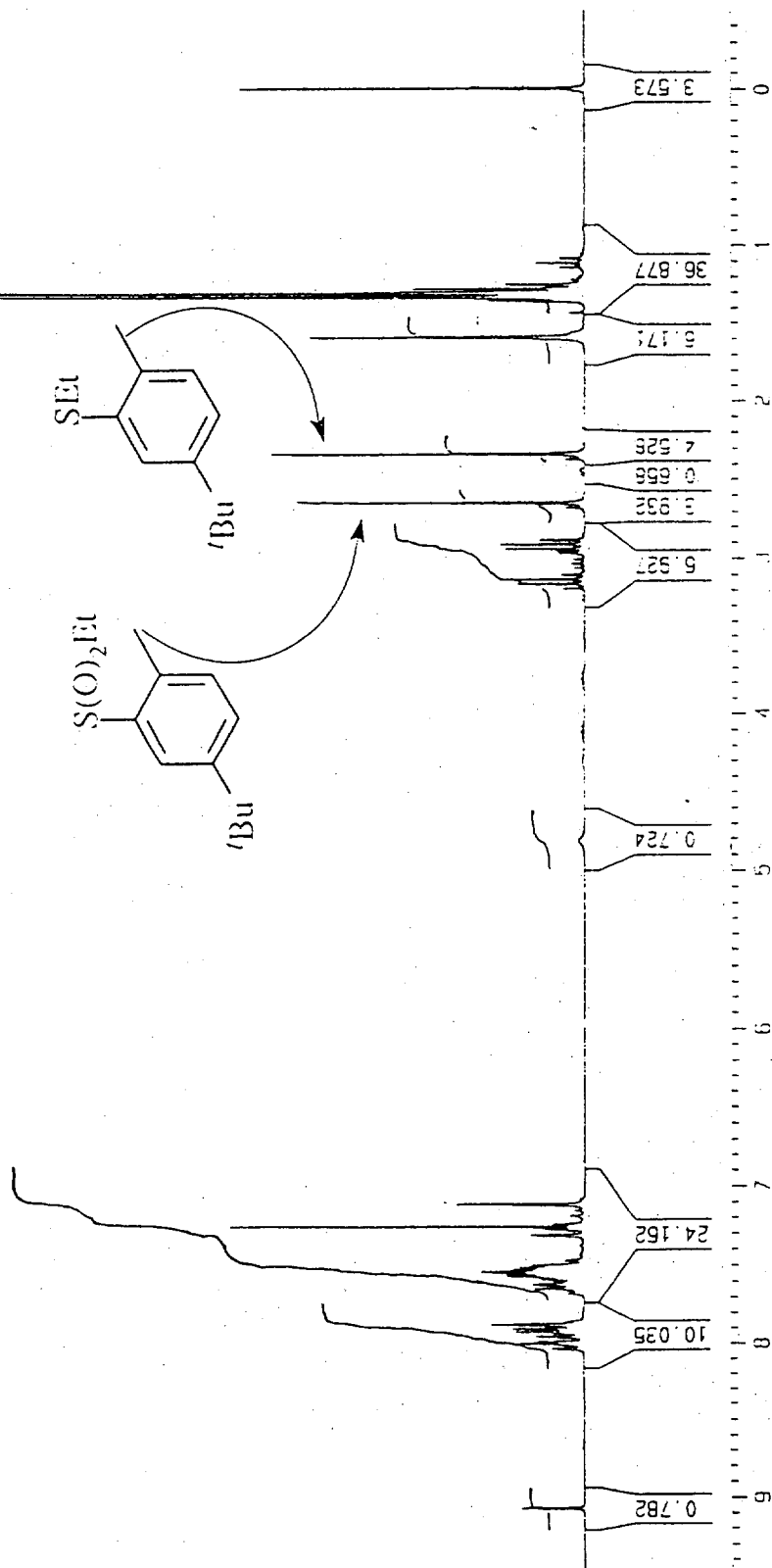
Reaction of benzaldehyde, imine, benzenesulfonamide, PhSO₂NHEt.
 of O-alkylation product.

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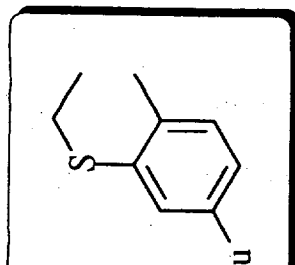
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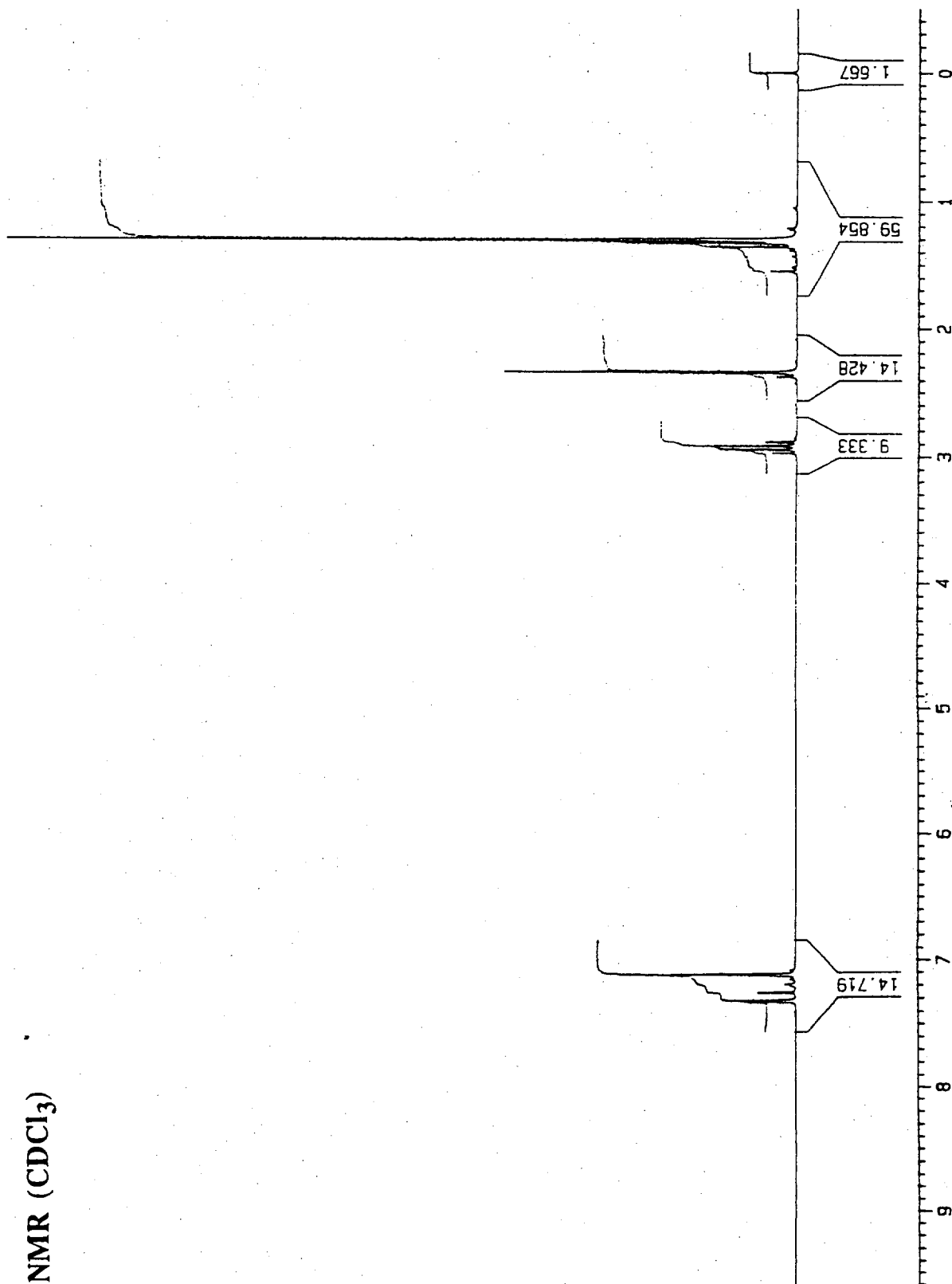
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NMR (CDCl₃)



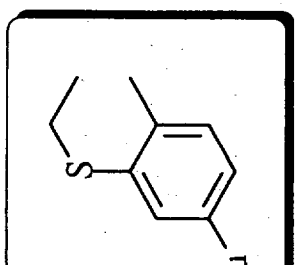
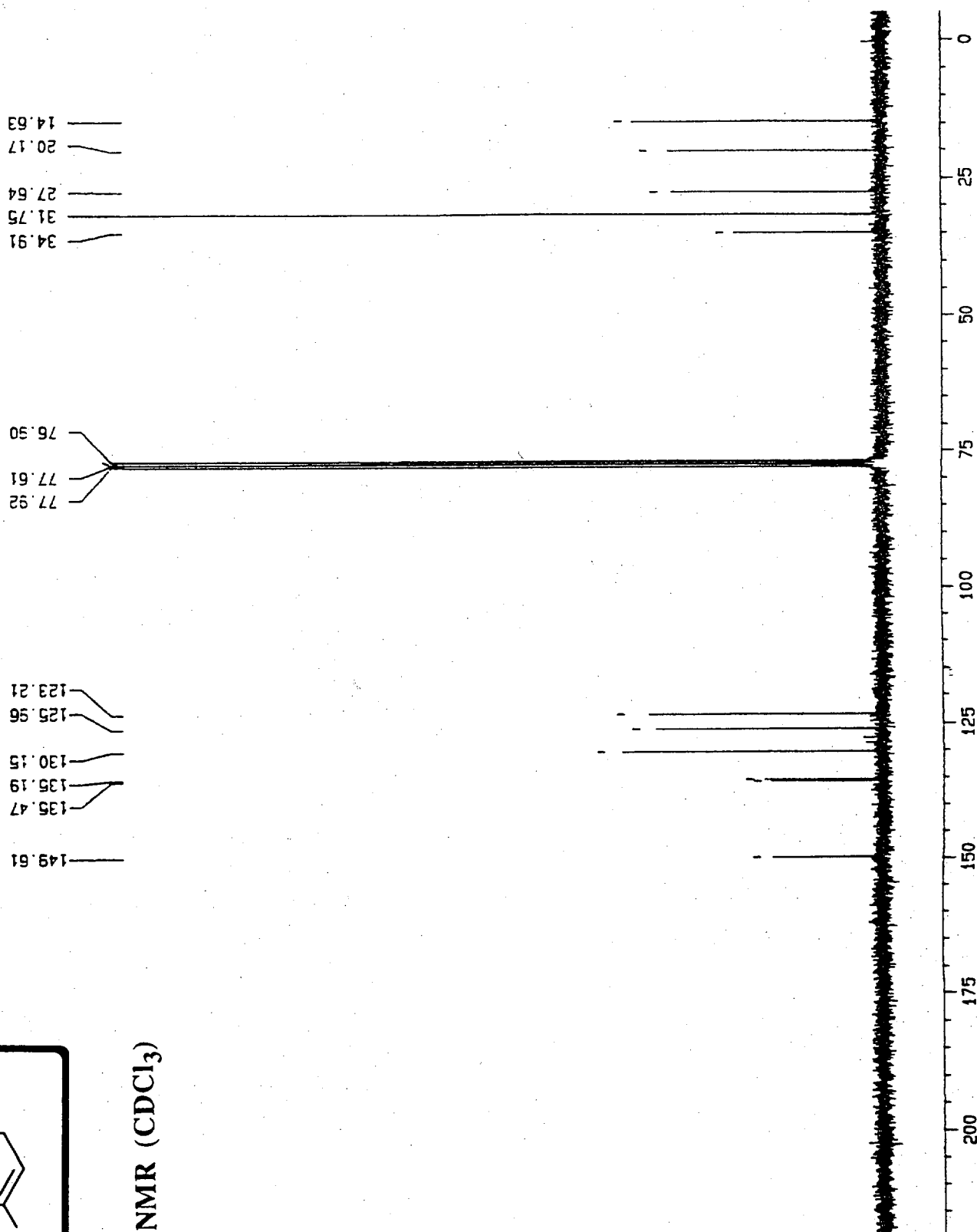
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 FIDRES 0.249327 H
 AQ 2.0054517 s
 RG 9195.2
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NMR (CDCl₃)

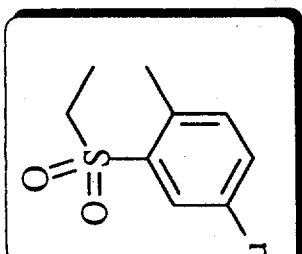
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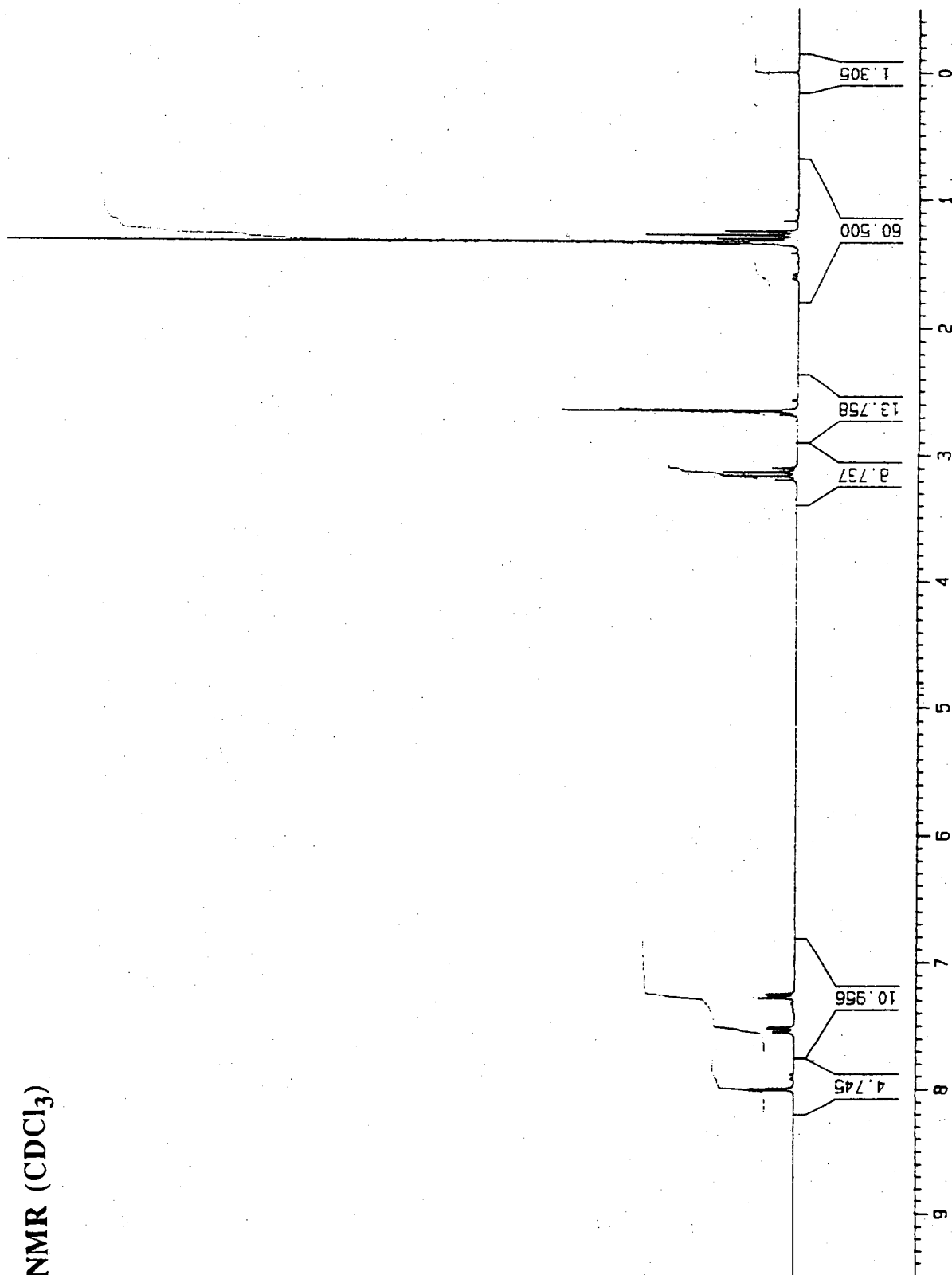
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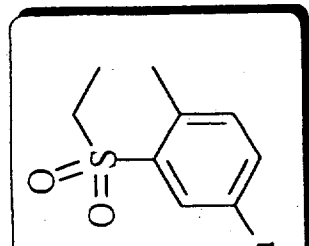
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¹H NMR (CDCl₃)





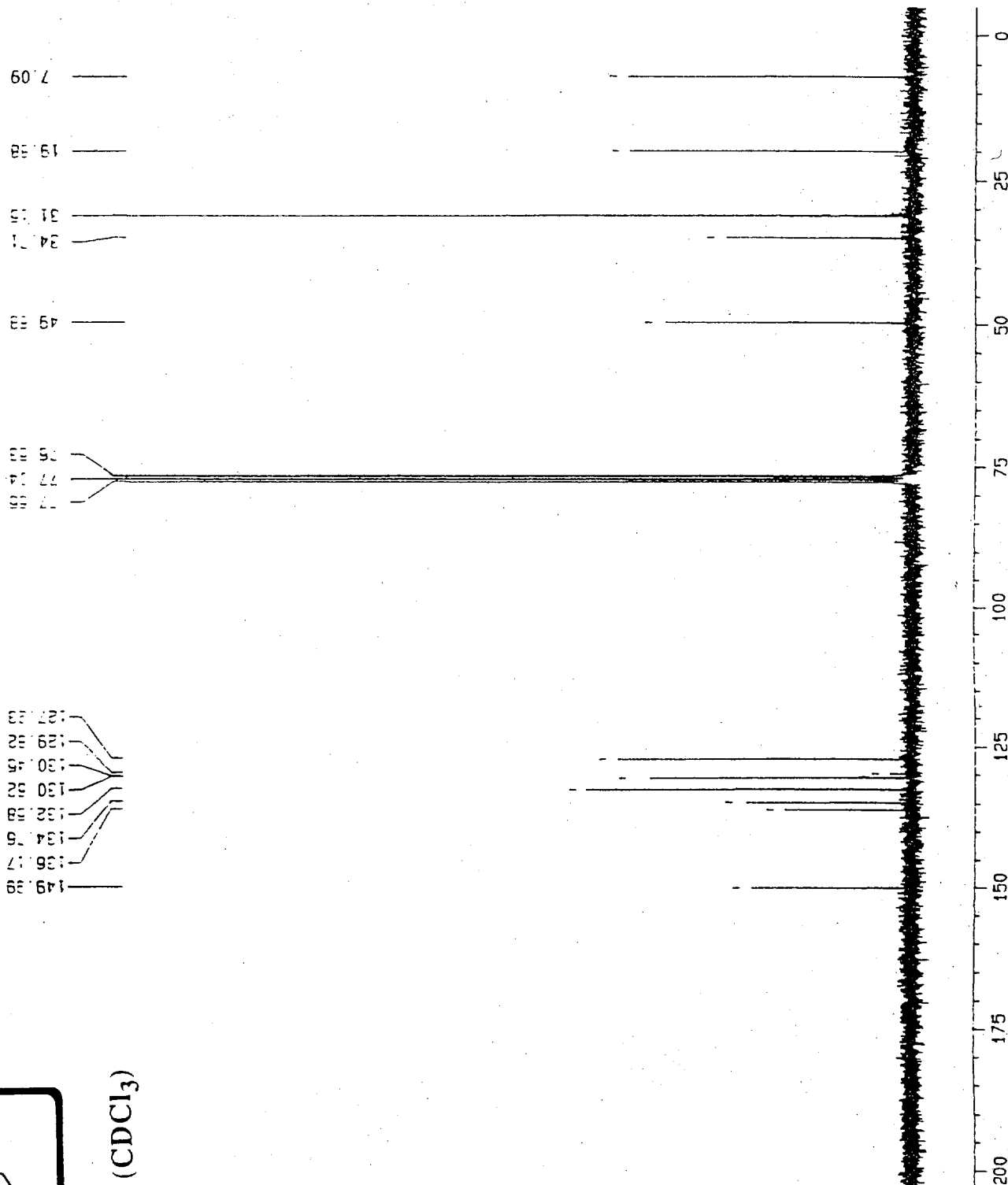
NMR (CDCl₃)

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 AQ 2.0054517 s
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1D NMR plot parameters
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 F1 14465.90 H
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 HZCH 671.83551 H



D₂O

¹H NMR (D₂O)

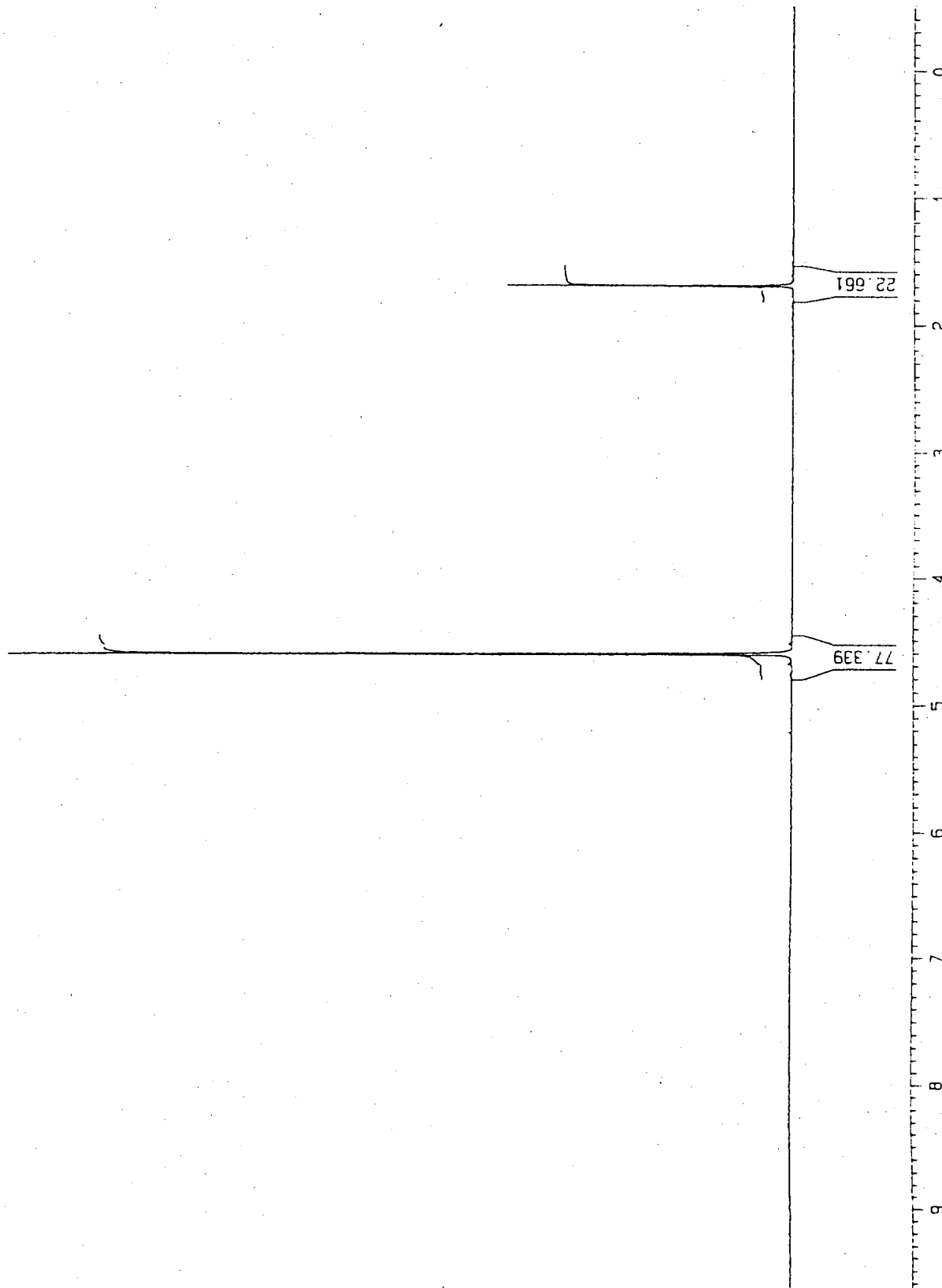
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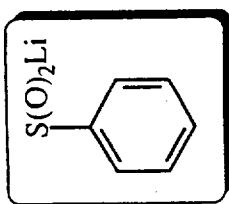
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7





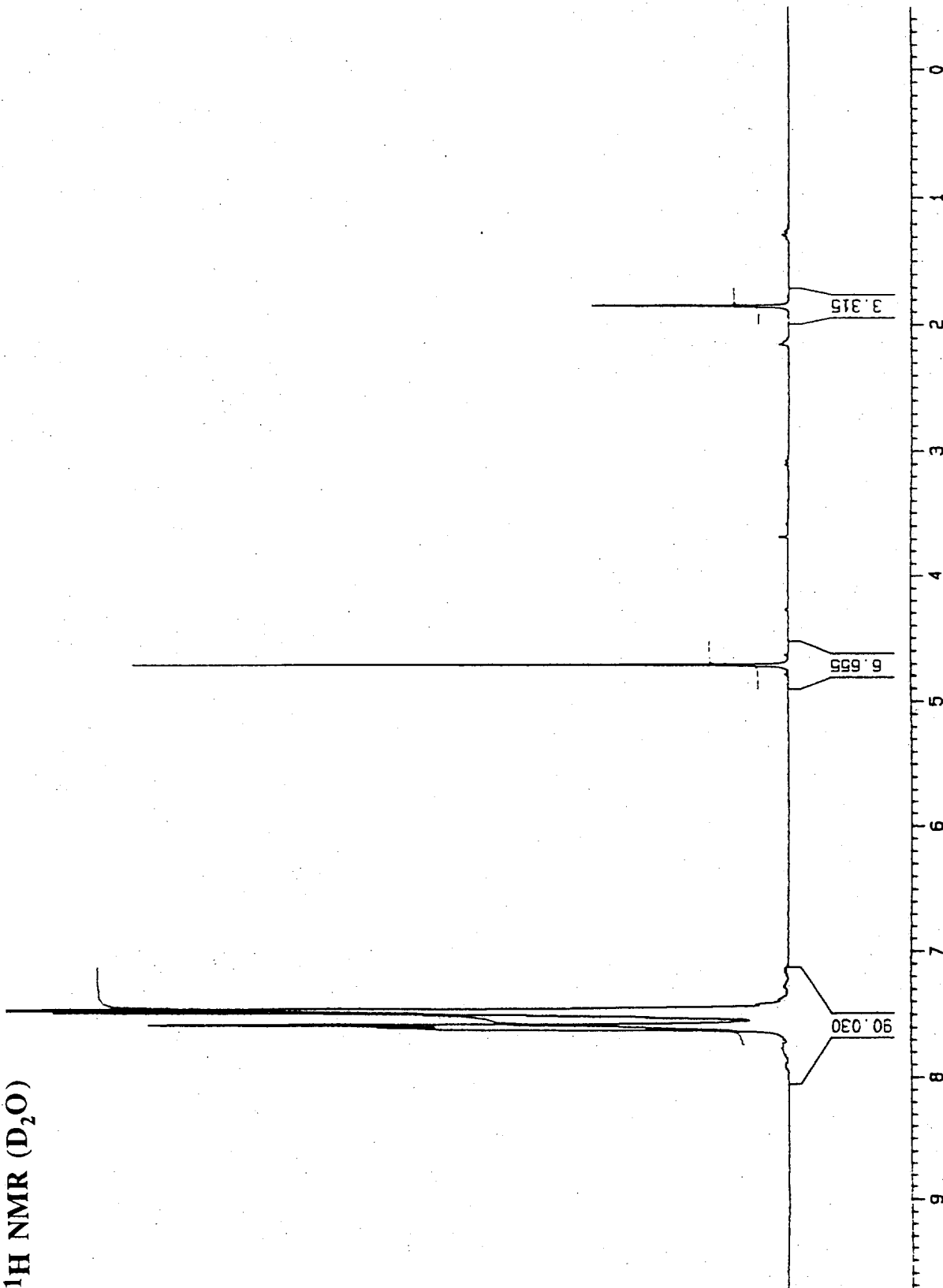
¹H NMR (D₂O)

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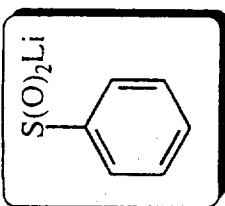
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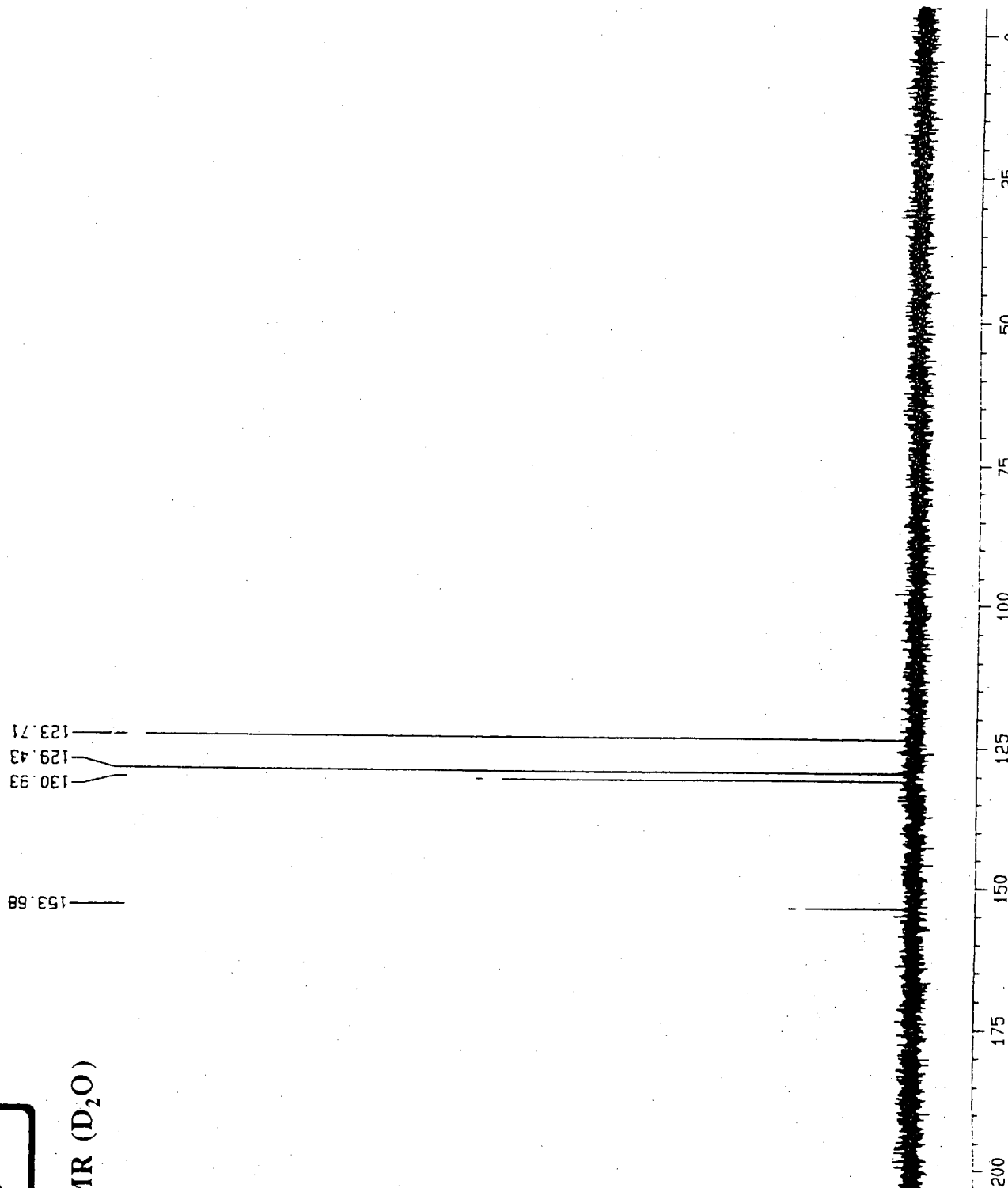
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 HZCM 119.36022 Hz



8



¹³C NMR (D₂O)



Current Data Parameters
 NAME vcb13
 EXPNO 10
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F2 - Acquisition Parameters
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 TE 300.0 K
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 PCPO2 100.00 u
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 MUC2 1H
 PL2 -6.00 d
 D1 2.00000000 s
 P1 5.00 u
 SF01 62.9027614 H
 MUC1 13C
 PL1 -6.00 d

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1D NMR plot parameters
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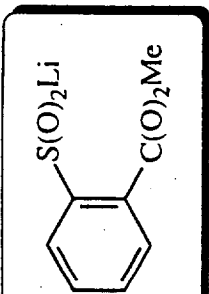
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 PL1 -6.00 dB

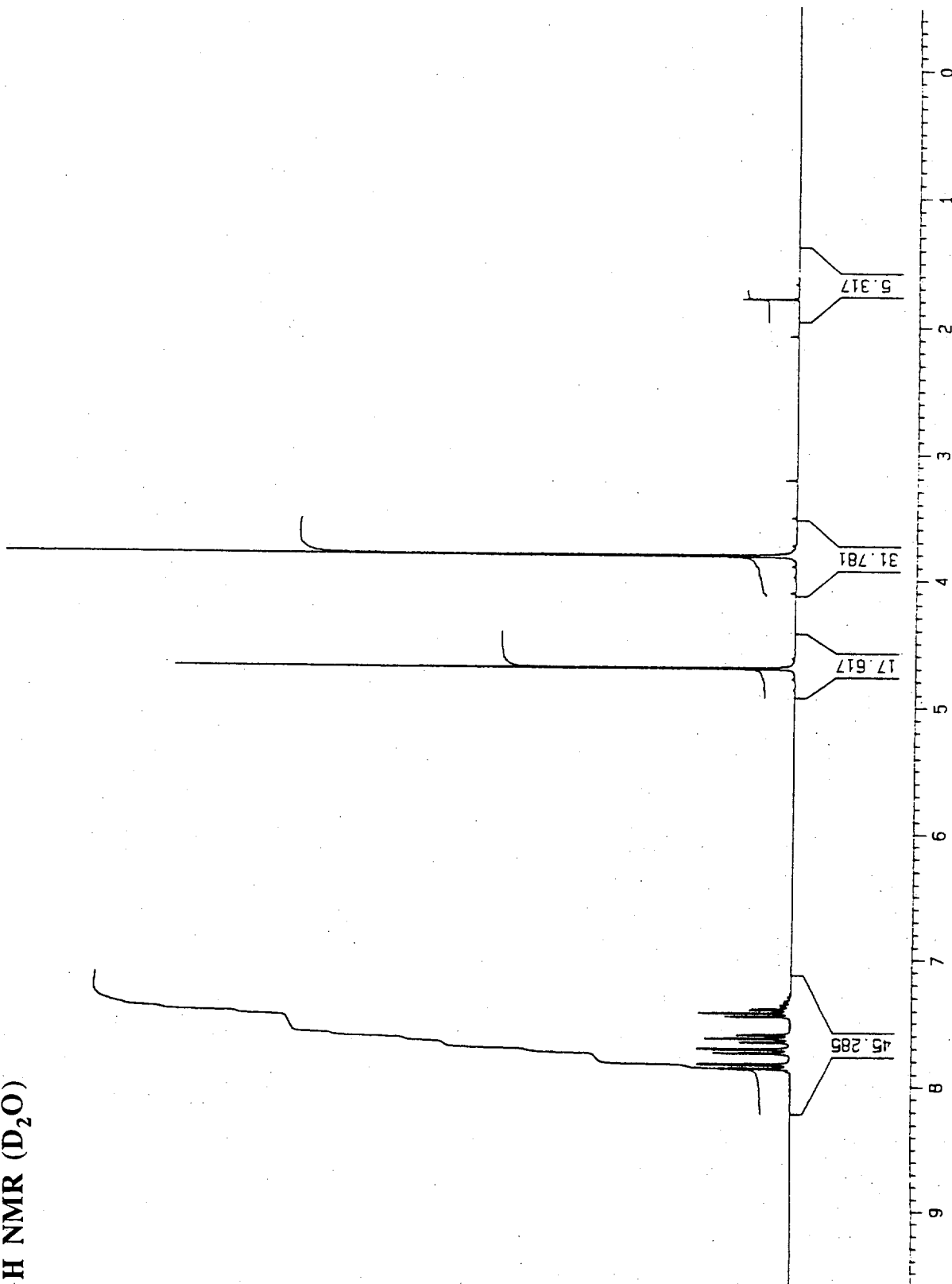
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1D NMR plot parameters
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10



H NMR (D₂O)



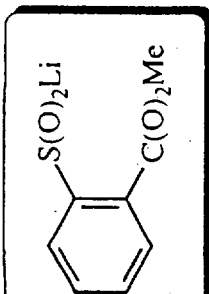
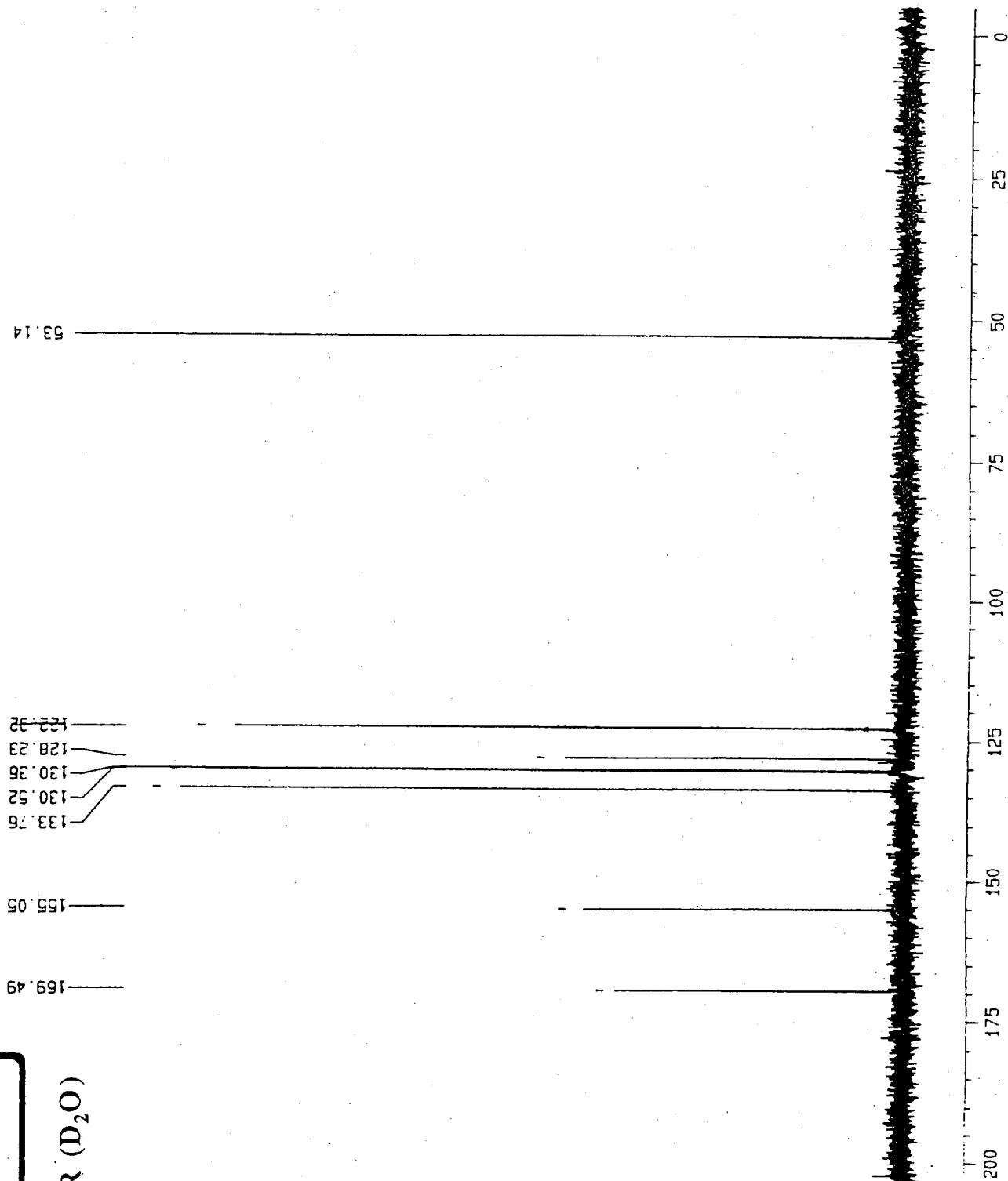
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 AQ 2.0054517 s
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 TE 300.0 K
 D11 0.03000000 s
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 SF02 250.1312506 M
 NUC2 1H
 PL2 -6.00 d
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 SF01 62.9027614 M
 NUC1 13C
 PL1 -6.00 d

F2 - Processing parameter
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1D NMR plot parameters
 CX 22.00 c
 FIP 230.000 p
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(11)



¹³C NMR (D₂O)

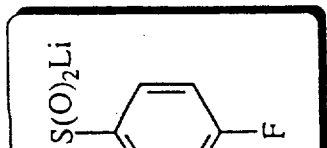
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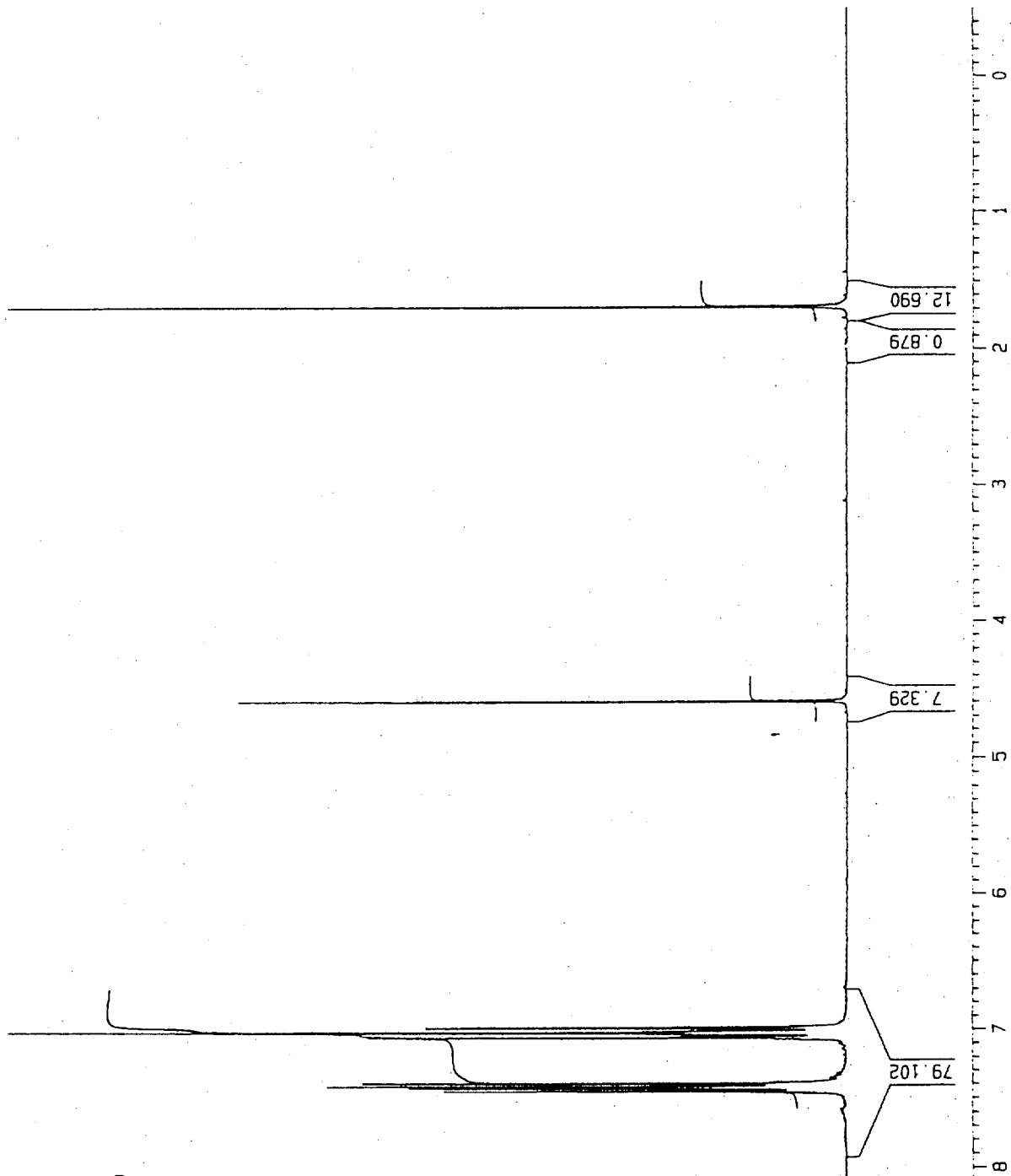
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 RG 1024
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10 NMR plot parameters
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MR (D₂O)



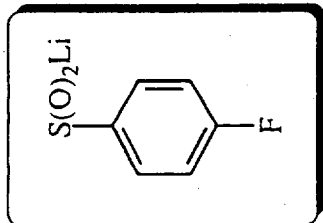
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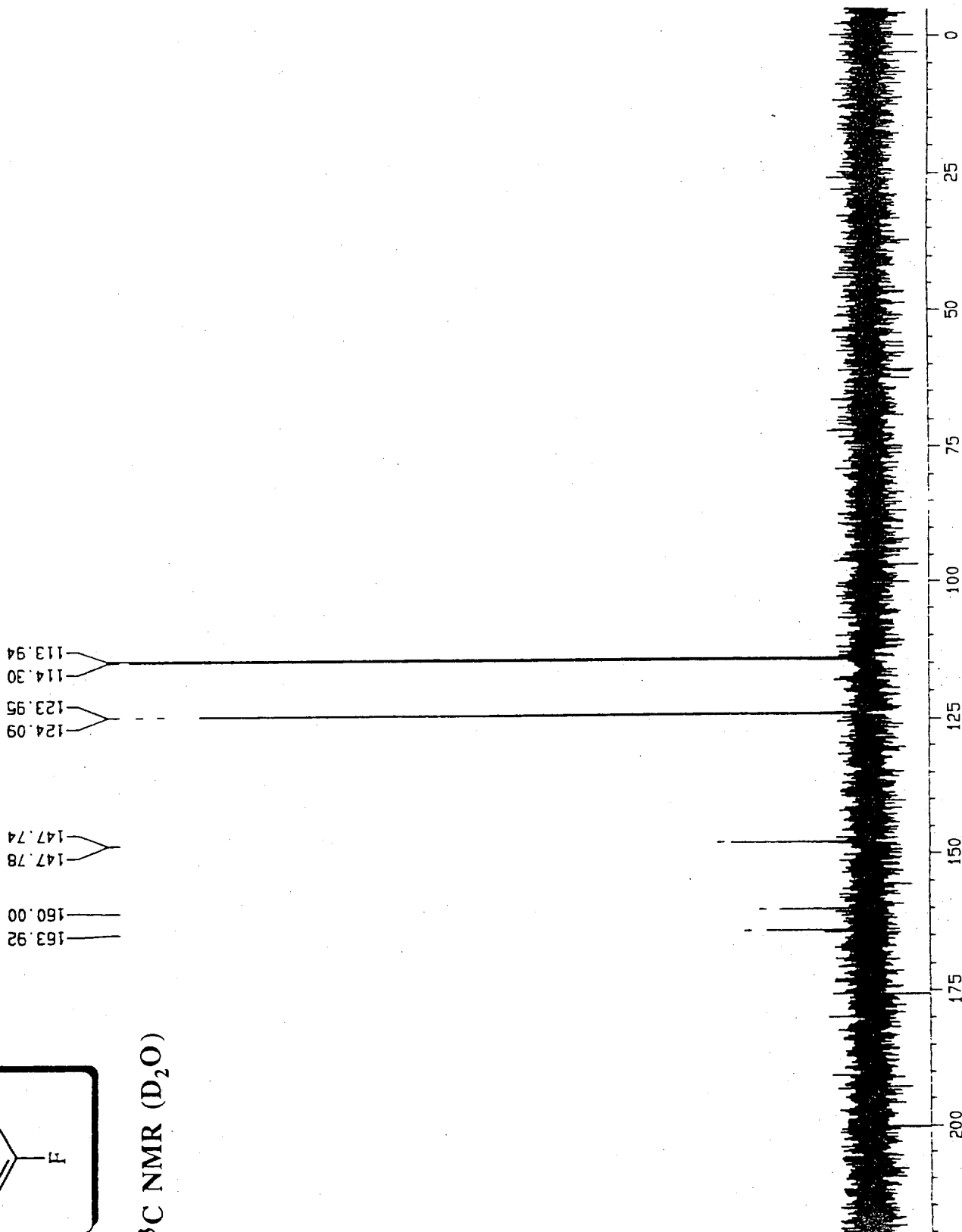
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 AQ 2.0054517 s
 RG 2298.8
 DW 30.600 U
 DE 10.00 U
 TE 300.0 K
 D11 0.03000000 s
 PL12 18.00 d
 CPOPRG2 waltz16
 PCPD2 100.00 U
 SF02 250.1312506 M
 NUC2 1H
 PL2 -6.00 d
 D1 2.00000000 s
 P1 5.00 U
 SF01 62.9027614 M
 NUC1 13C
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1D NMR plot parameters
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 F1P 230.000 p
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¹³C NMR (D₂O)



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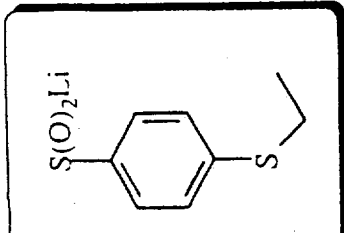
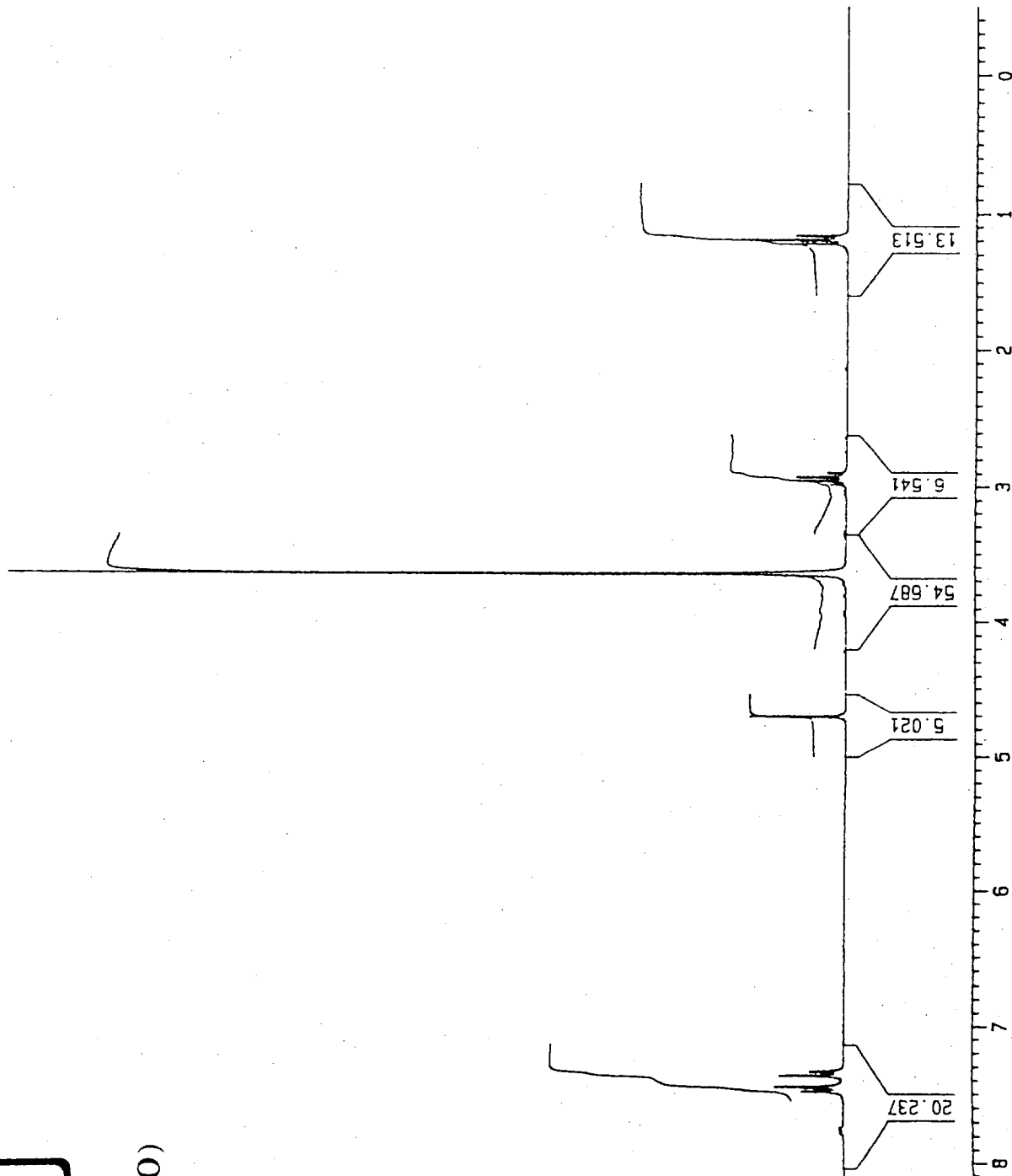
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1D NMR plot parameters
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 F1P 10.000 P
 F1 2501.30 H
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 HZCM 119.36022 H

Dioxane



¹H NMR (D₂O)

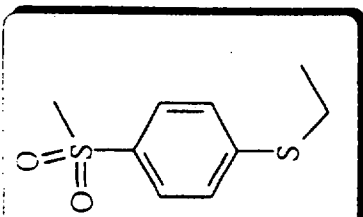
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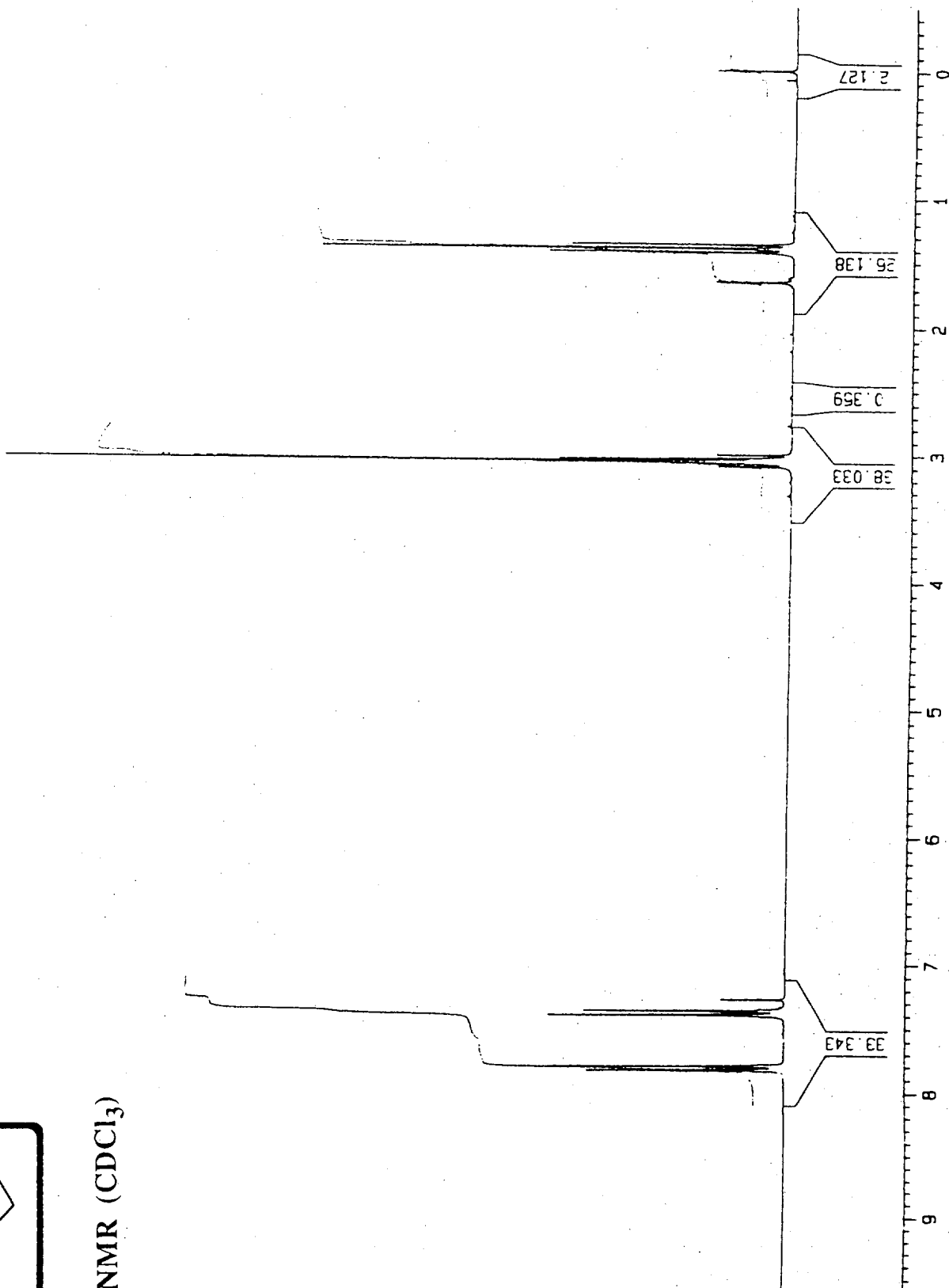
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15



NMR (CDCl₃)



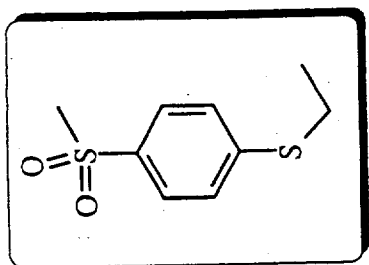
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 PROCNO 1

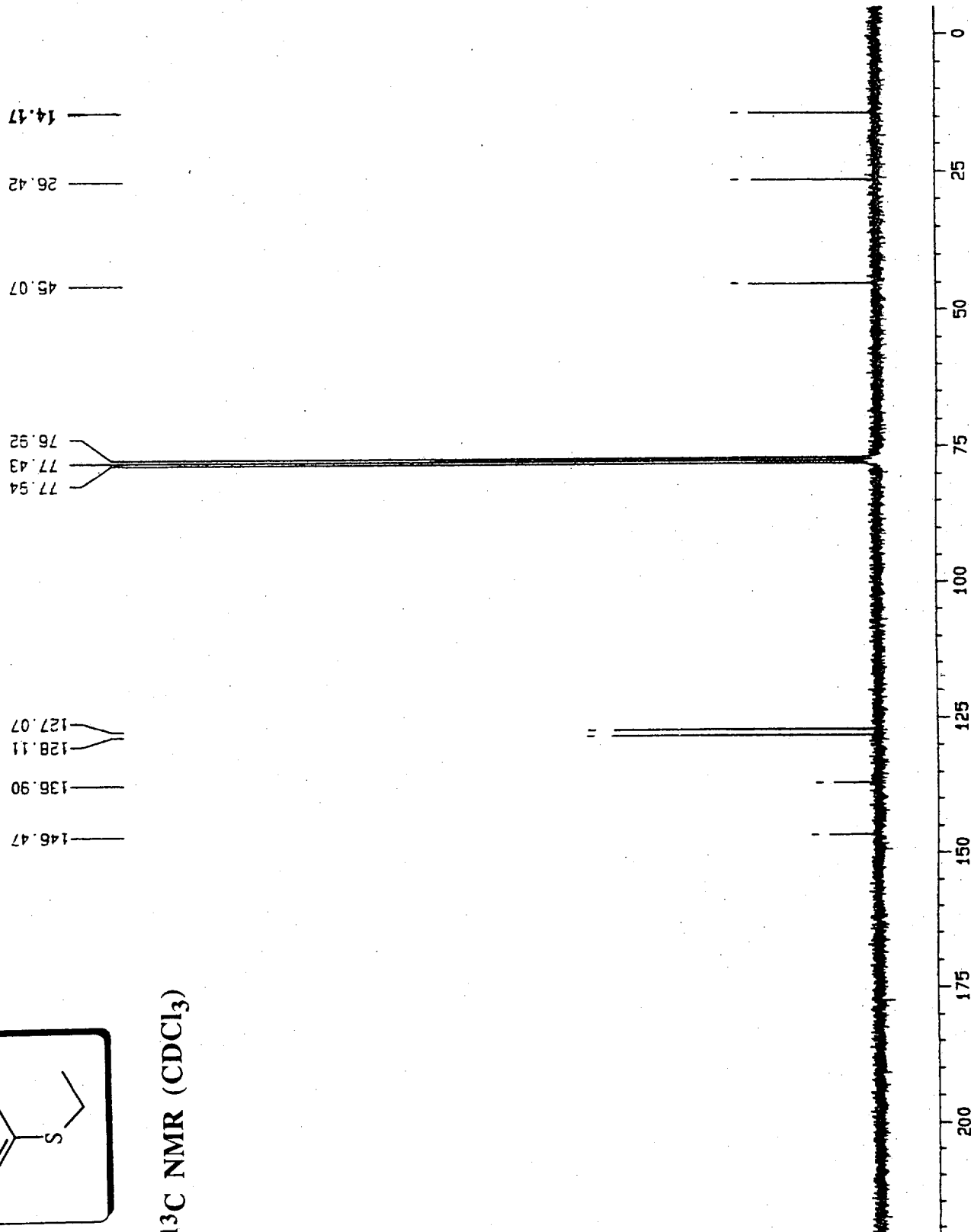
F2 - Acquisition Parameters
 Date_ 980609
 Time 10:55
 INSTRUM spect
 PROBHD 5 mm QNP 1H/1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 1024
 DS 0
 SWH 16339.869 H
 FIDRES 0.249327 H
 AQ 2.0054517 s
 RG 9195.2
 DM 30.600 u
 DE 10.00 u
 TE 300.0 K
 D11 0.03000000 s
 PL12 18.00 d
 CPOPRG2 waltz16
 PCPD2 100.00 u
 SF02 250.1312506 M
 NUC2 1H
 PL2 -6.00 d
 D1 2.00000000 s
 P1 5.00 u
 SF01 62.9027614 H
 NUC1 13C
 PL1 -6.00 d

F2 - Processing parameters
 SI 32768
 SF 62.8952134 H
 XDM EM
 SSB 0
 LB 0.80 H
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 22.00 c
 F1P 230.000 p
 F1 14465.90 H
 F2P -5.000 p
 F2 -314.48 H
 PPMCH 10.68182 p
 HZCH 671.83527 H



¹³C NMR (CDCl₃)



Current Data Parameters
 NAME feb34pm
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameter

Date_ 980921
 Time 12.10
 INSTRUM spect
 PROBHD 5 mm QNP 1H/1
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SH 4990.020 Hz
 FIDRES 0.162283 Hz
 AQ 3.2834036 s
 RG 512
 DM 100.200 u
 DE 10.00 u
 TE 300.0 K
 D1 2.0000000 s
 P1 7.50 u
 SF01 250.1318626 MHz
 NUC1 1H
 PL1 -6.00 dB

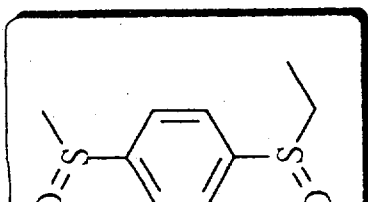
F2 - Processing parameter

SI 16384
 SF 250.1300012 MHz
 MDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

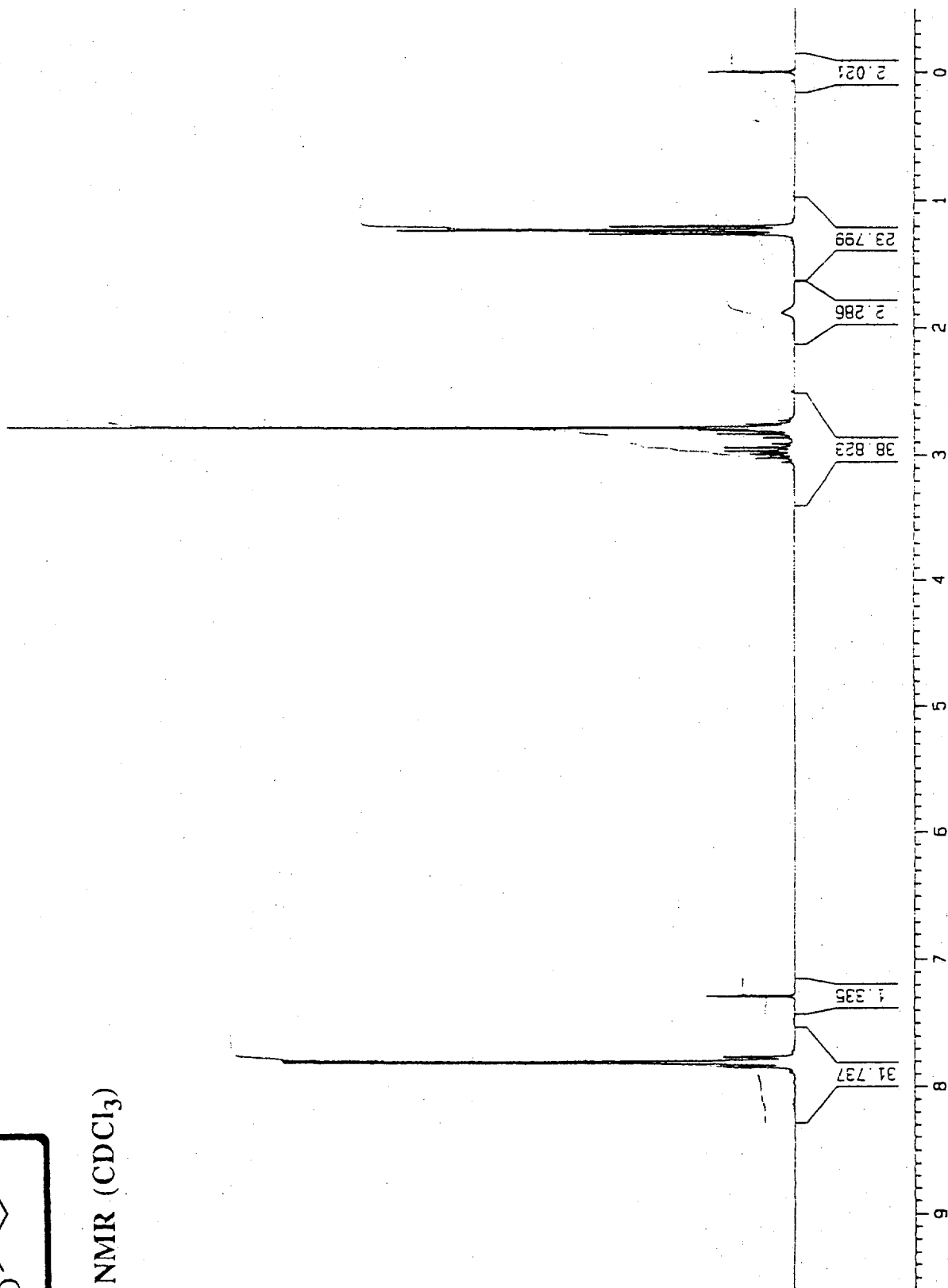
1D NMR plot parameters

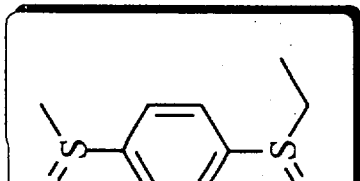
CX 22.00 ci
 FIP 10.000 pf
 F1 2501.30 Hz
 F2P -0.500 pf
 F2 -125.05 Hz
 PPMCM 0.47727 pf
 HZCM 119.38022 Hz

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NMR (CDCl₃)





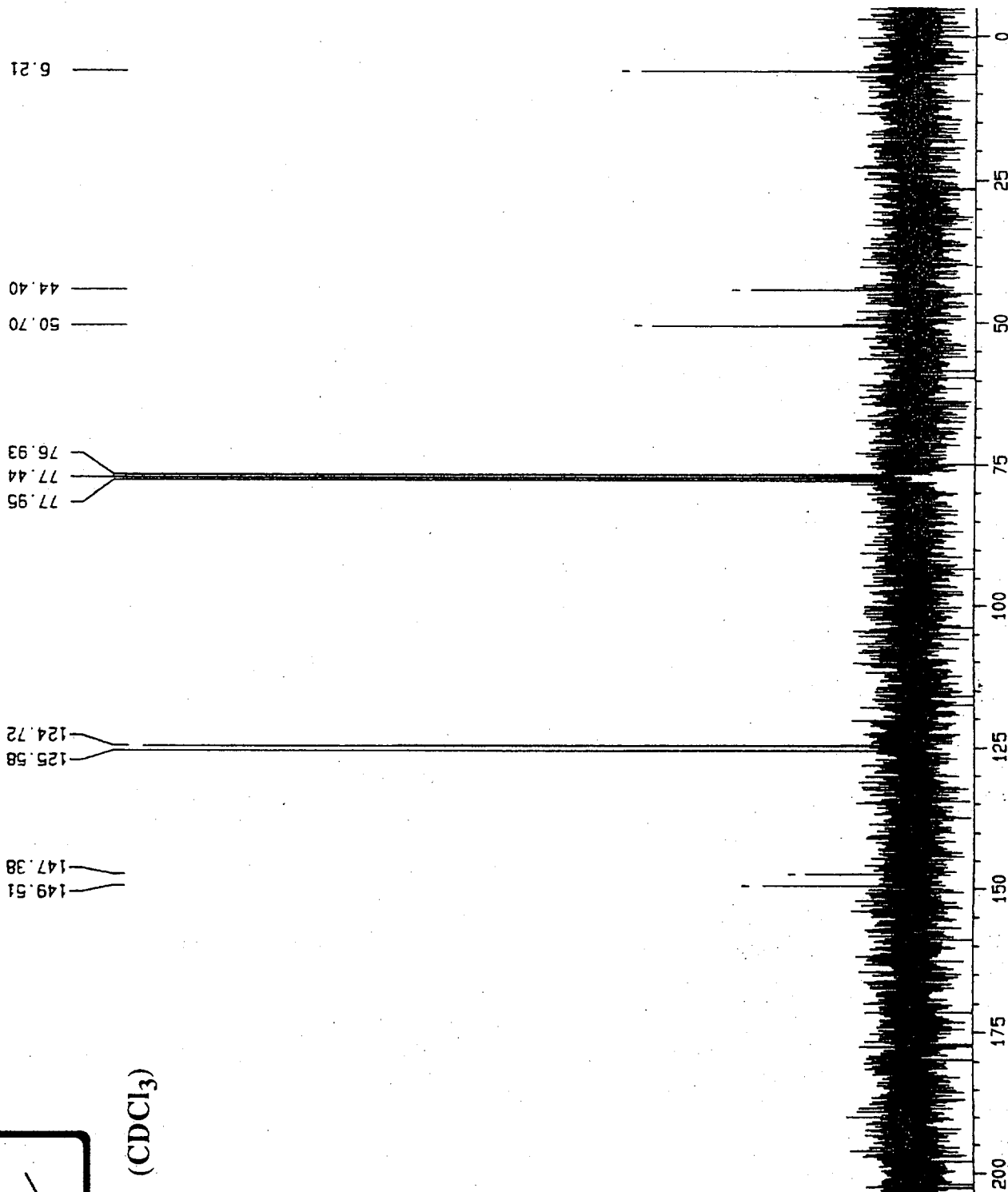
NMR (CDCl₃)

Current Data Parameters
 NAME fab34bm
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 980921
 Time 12.19
 INSTRUM spect
 PROBHD 5 mm QNP 1H/1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl₃
 NS 120
 DS 0
 SWH 16339.869 H
 FIDRES 0.249327 H
 AQ 2.0054517 s
 RG 2298.8
 DM 30.600 u
 DE 10.00 u
 TE 300.0 K
 D11 0.0300000 s
 PL12 18.00 d
 CPOPRG2 waltz16
 PCPD2 100.00 u
 SF02 250.1312506 M
 NUC2 1H
 PL2 -6.00 d
 D1 -6.00 d
 P1 2.0000000 s
 SF01 62.9027614 M
 NUC1 13C
 PL1 -6.00 d

F2 - Processing parameters
 SI 32768
 SF 62.8952140 M
 MDW EM
 SSB 0
 LB 0.80 H
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 22.00 c
 F1P 230.000 p
 F1 14465.90 H
 F2P -5.000 d
 F2 -314.48 H
 PPMCM 10.68182 p
 HZCM 671.83527 H



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