

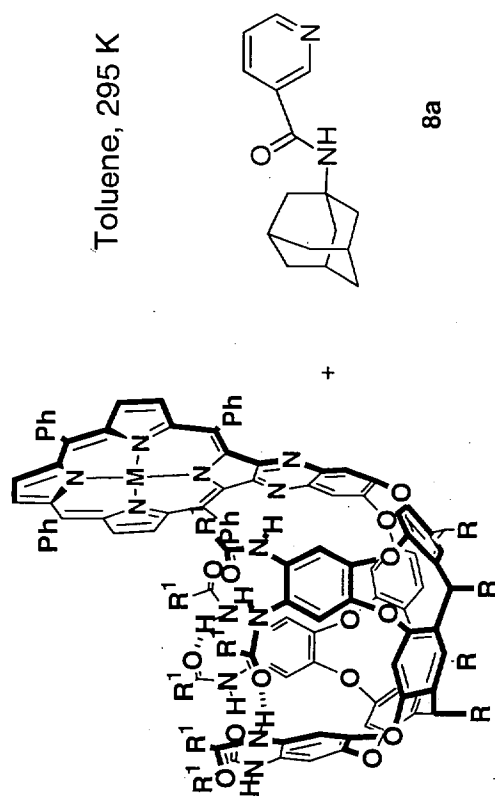
Supporting Information

A Cavitand-Porphyrin Hybrid

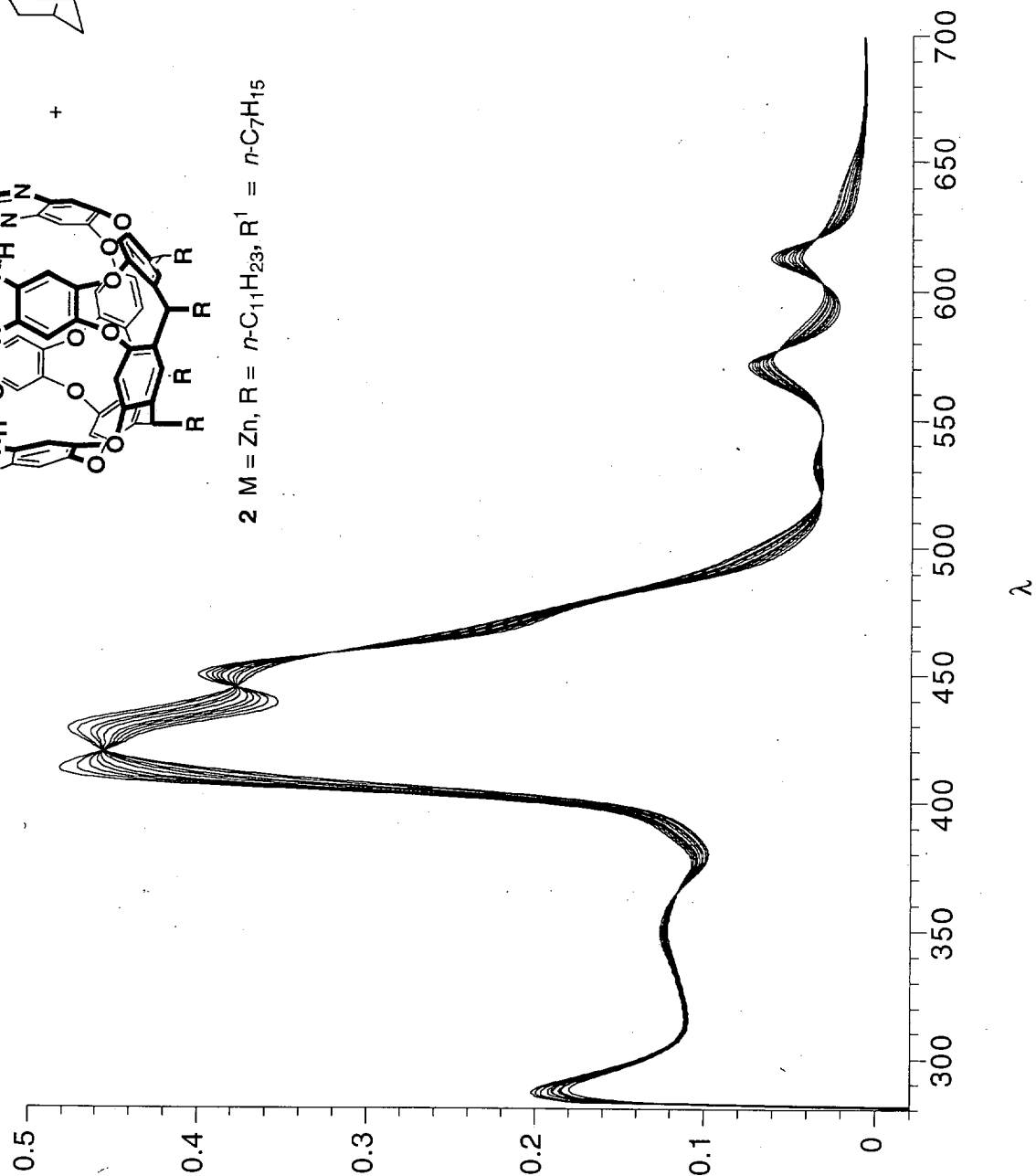
Stephen D. Starnes, Dmitry M. Rudkevich, and Julius Rebek, Jr.

The Skaggs Institute for Chemical Biology and The Department of Chemistry, The Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, California 92037

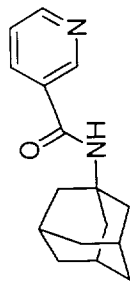
General. All compounds synthesized were characterized by FTIR, high-resolution ^1H and ^{13}C NMR spectroscopy and high-resolution mass-spectrometry (MALDI-FTMS). Pure amides **8a-e** and **9a,b** were obtained as colorless solids in 75-90% yields after crystallization, using textbook procedures of peptide chemistry. Compound **2** ($\text{M} = 2\text{H}$) was obtained as a purple solid in 43 % yield which was then metallated with $\text{Zn}(\text{OAc})_2$ in refluxing $\text{CHCl}_3/\text{MeOH}$ to give **2** ($\text{M} = \text{Zn}$) as a purple solid in 95 % yield. Complexation experiments were performed on a Bruker DRX-600 spectrometer (600 MHz) in toluene- d_8 and on a Perkin-Elmer UV-vis Lambda 12 spectrophotometer.



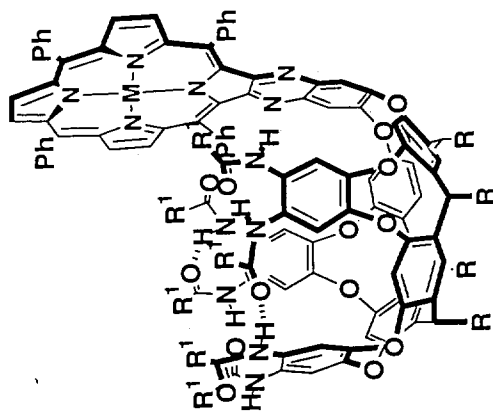
2 M = Zn, R = $n\text{-C}_{11}\text{H}_{23}$, R' = $n\text{-C}_7\text{H}_{15}$



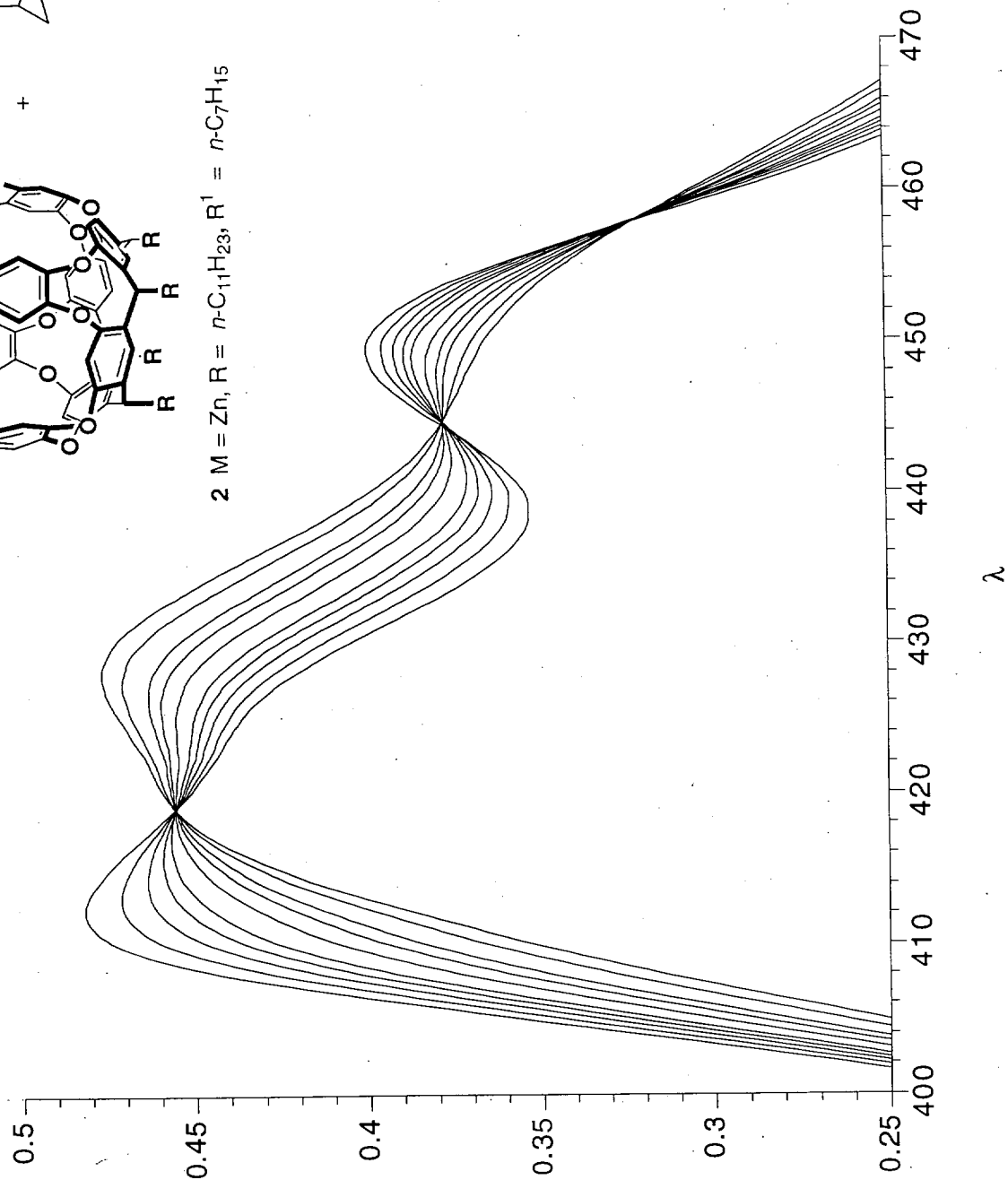
Toluene, 295 K



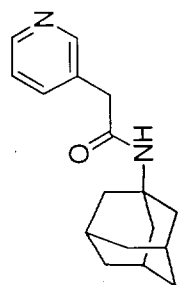
8a



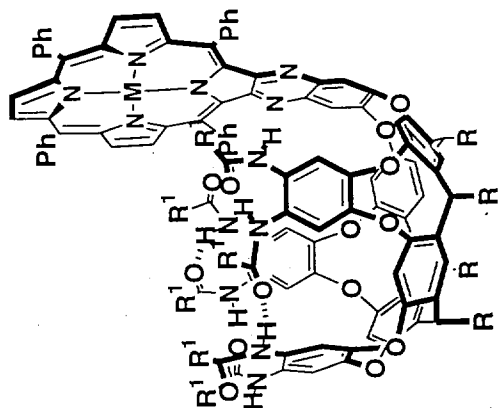
2 M = Zn, R = $n\text{-C}_{11}\text{H}_{23}$, R' = $n\text{-C}_7\text{H}_{15}$



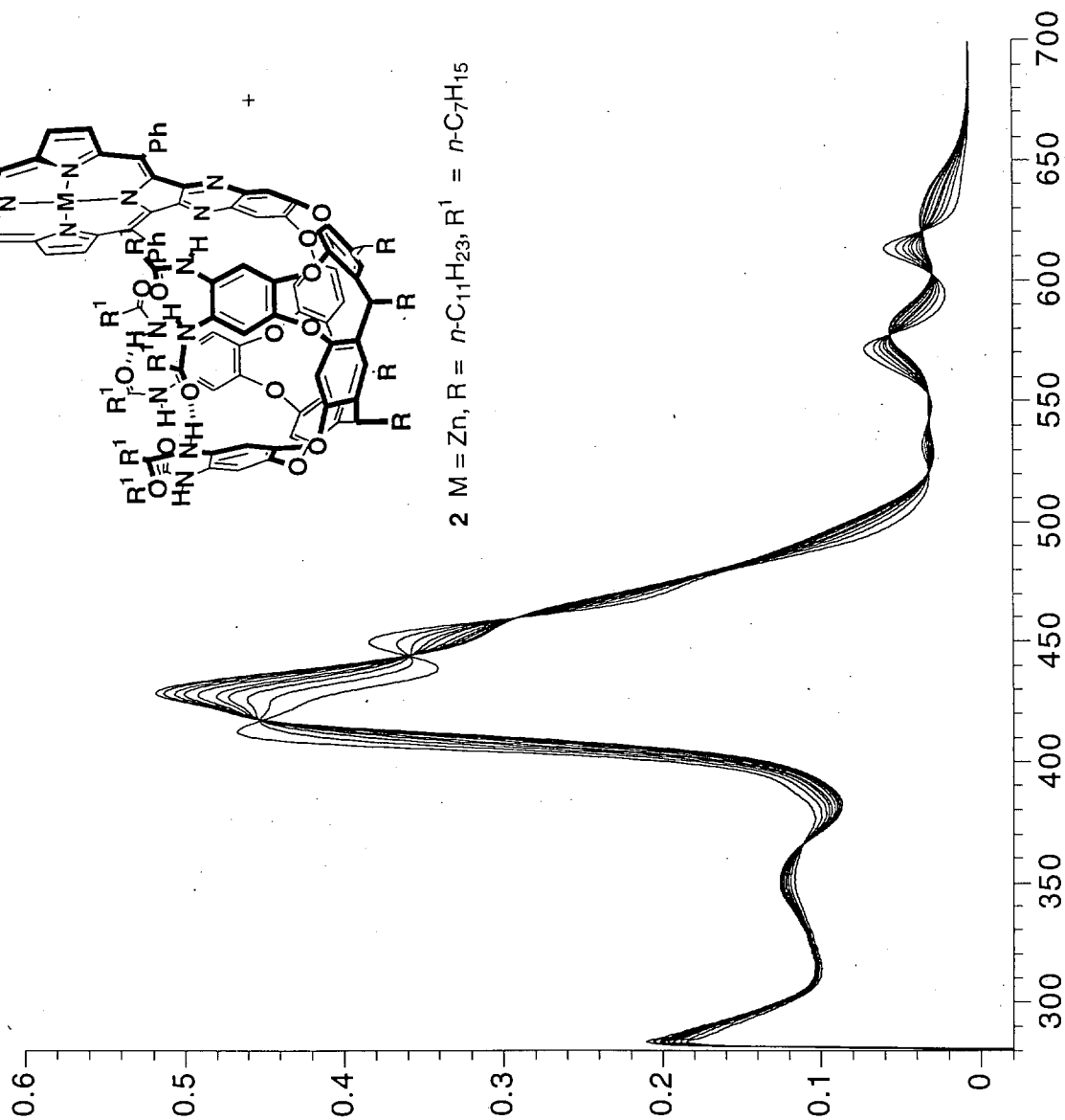
Toluene, 295 K



8b

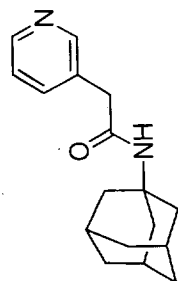


2 M = Zn, R = $n\text{-C}_{11}\text{H}_{23}$, $\text{R}^1 = n\text{-C}_7\text{H}_{15}$

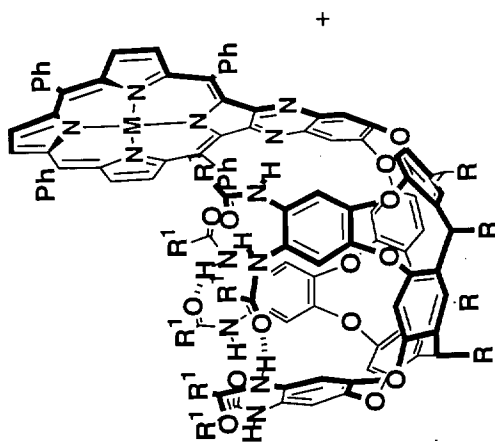


λ

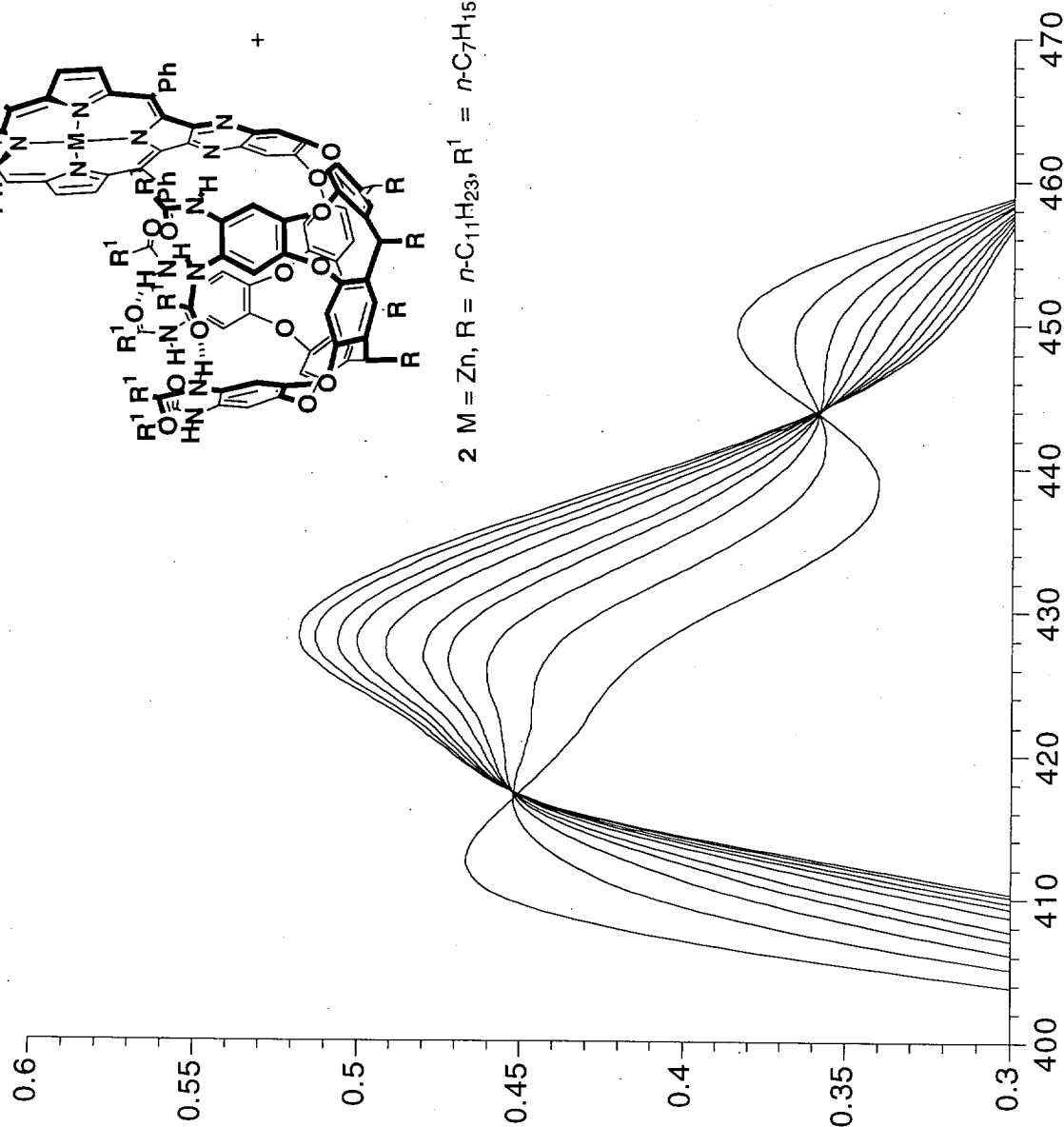
Toluene, 295 K



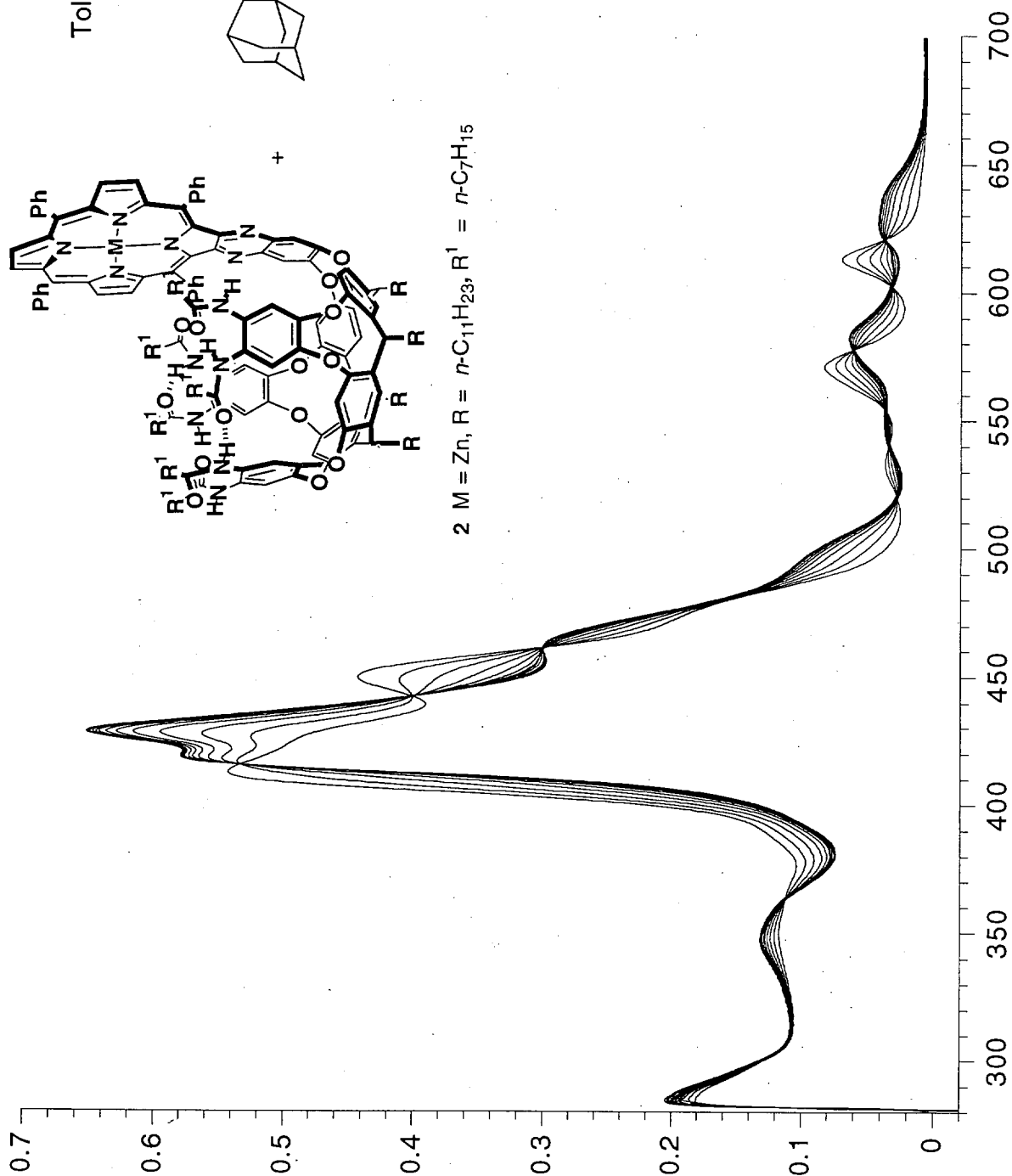
8b



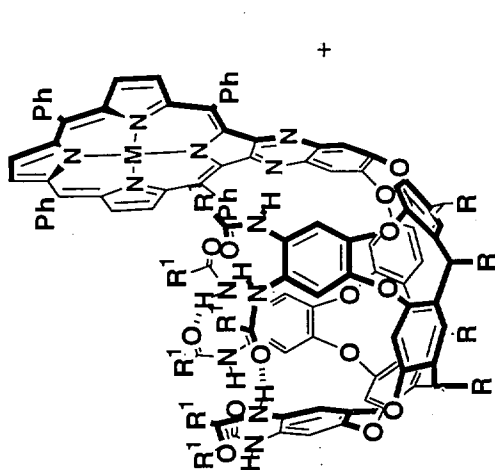
2 M = Zn, R = $n\text{-C}_{11}\text{H}_{23}$, $\text{R}' = n\text{-C}_7\text{H}_{15}$



λ

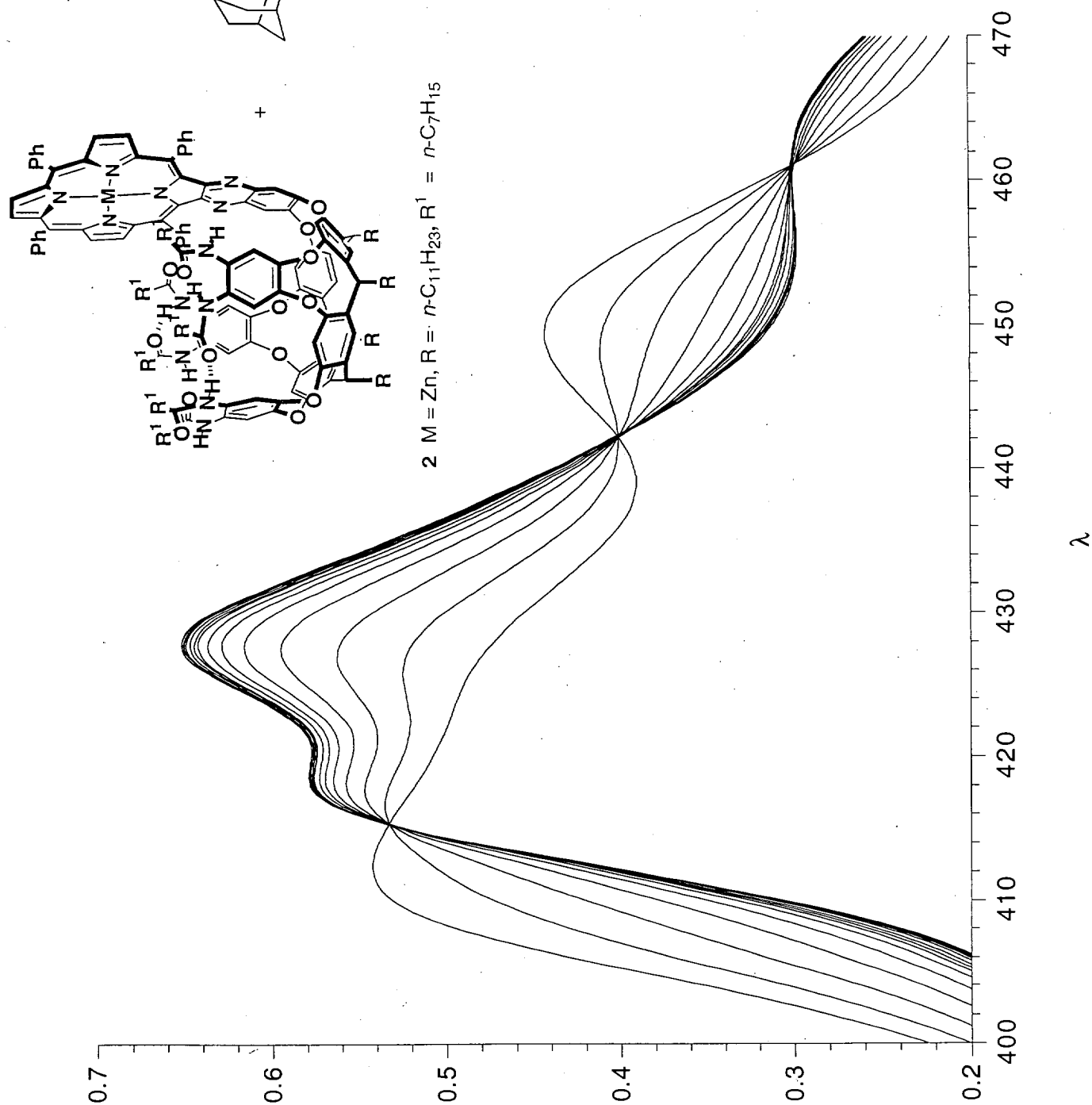


Toluene, 295 K



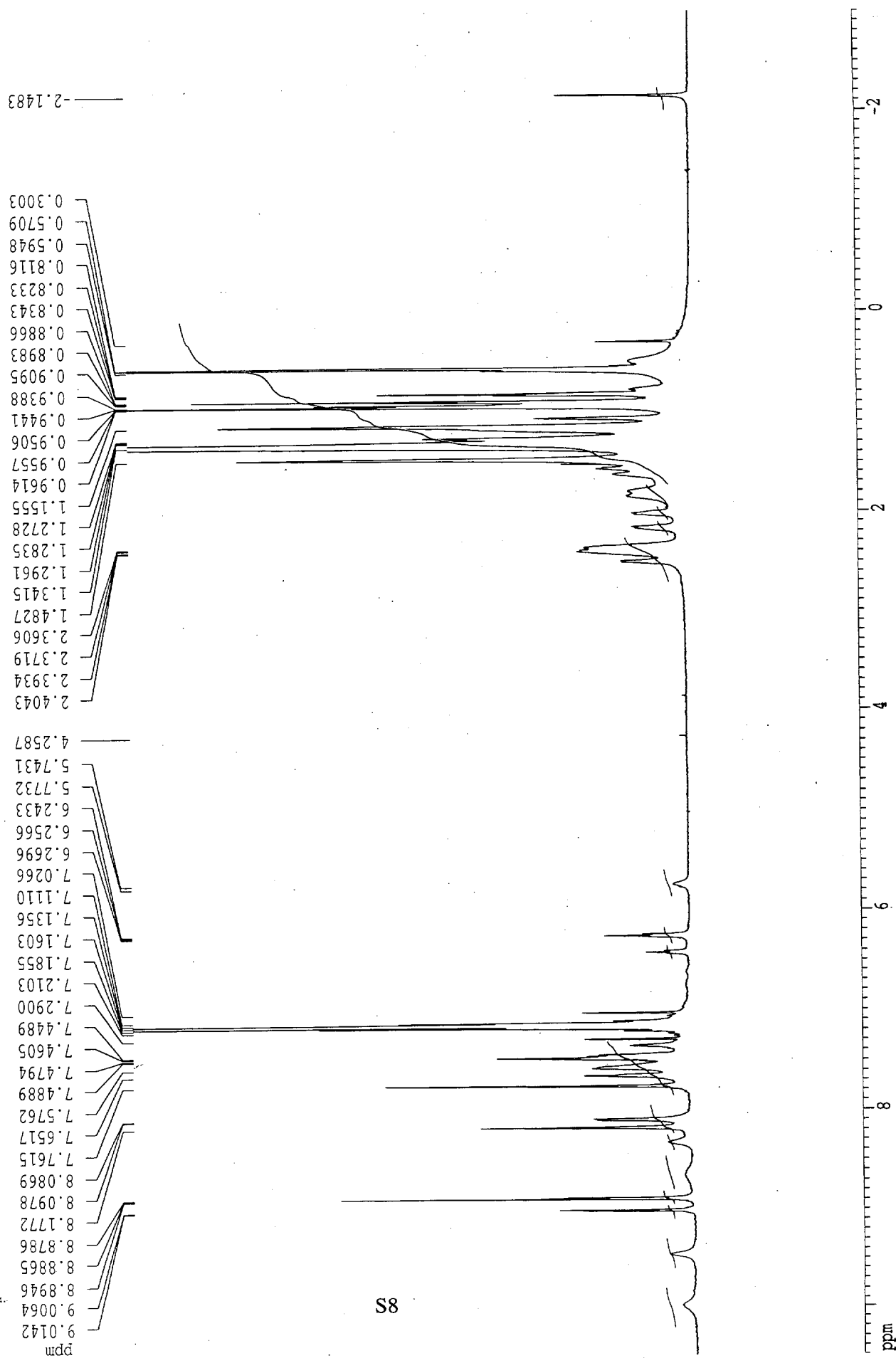
9b

2 M = Zn, R = n -C₁₁H₂₃, R¹ = n -C₇H₁₅

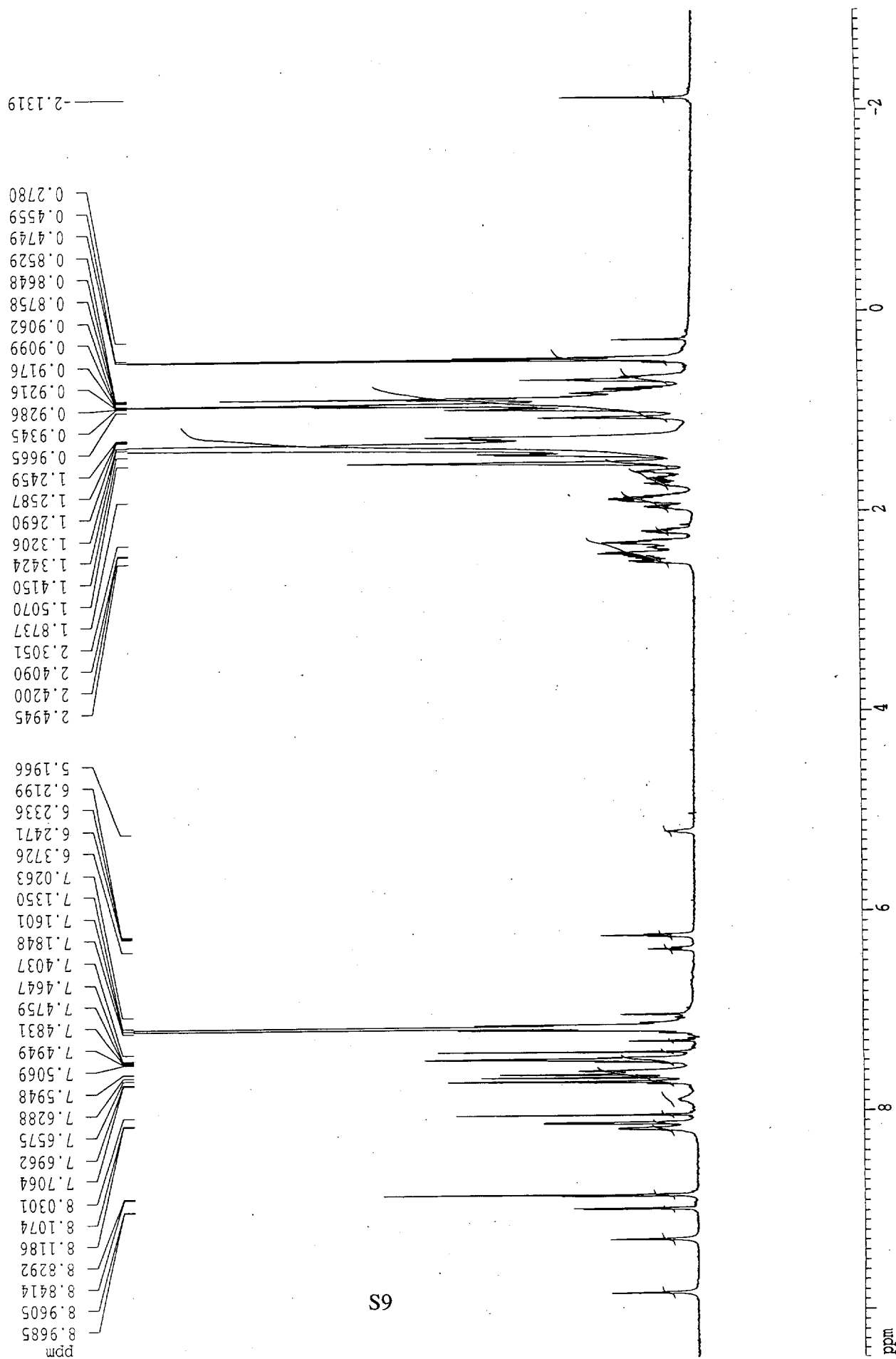


295 K
benzene- d_6

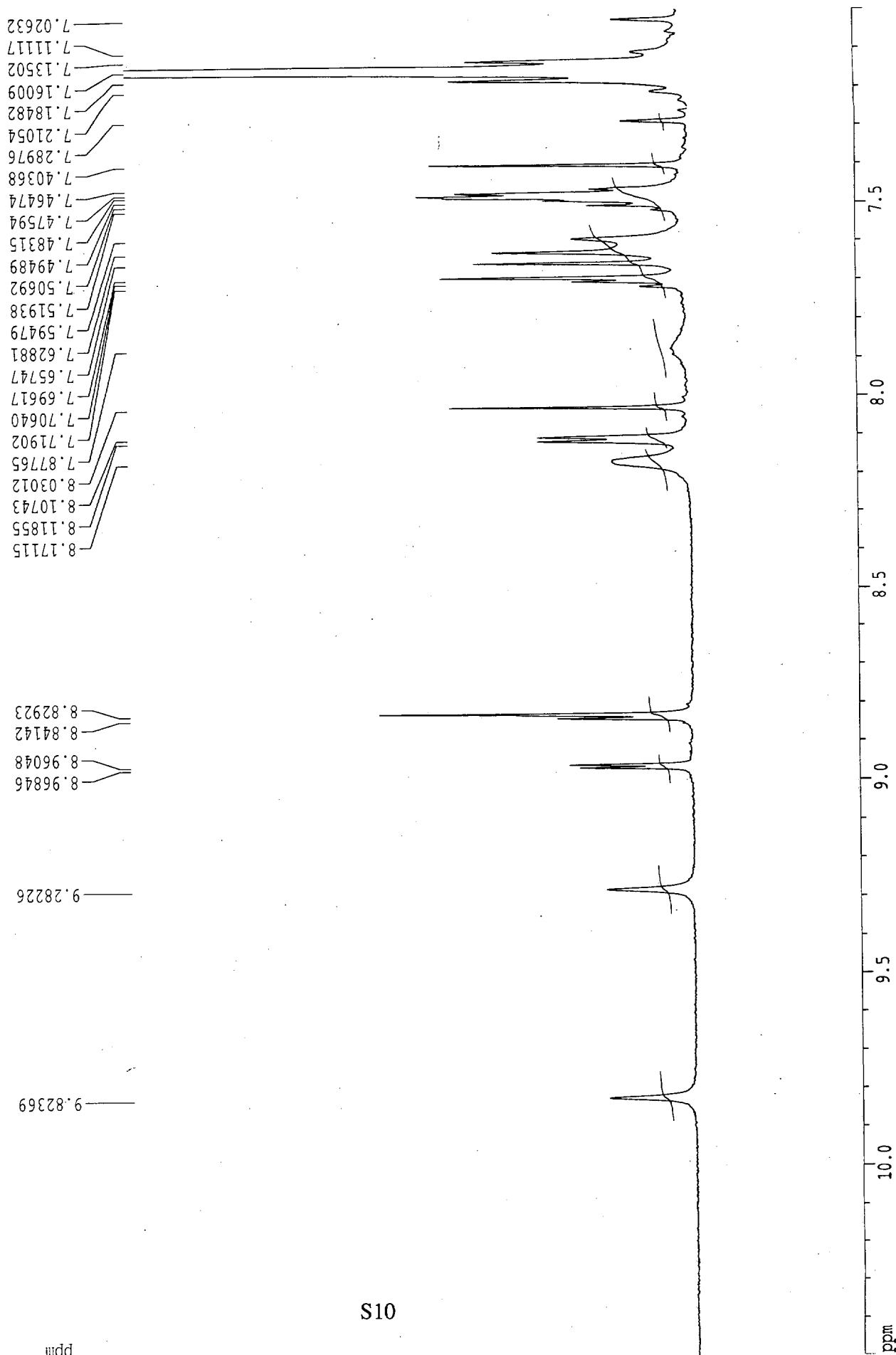
2 M = 2H, R = $n\text{-C}_{11}\text{H}_{23}$, $R^1 = n\text{-C}_7\text{H}_{15}$



2 M = 2H, R = $n\text{-C}_{11}\text{H}_{23}$, $\text{R}^1 = n\text{-C}_7\text{H}_{15}$ 330 K benzene- d_6



2 M = 2H, R = $n\text{-C}_{11}\text{H}_{23}$, R' = $n\text{-C}_7\text{H}_{15}$ 330 K benzene- d_6

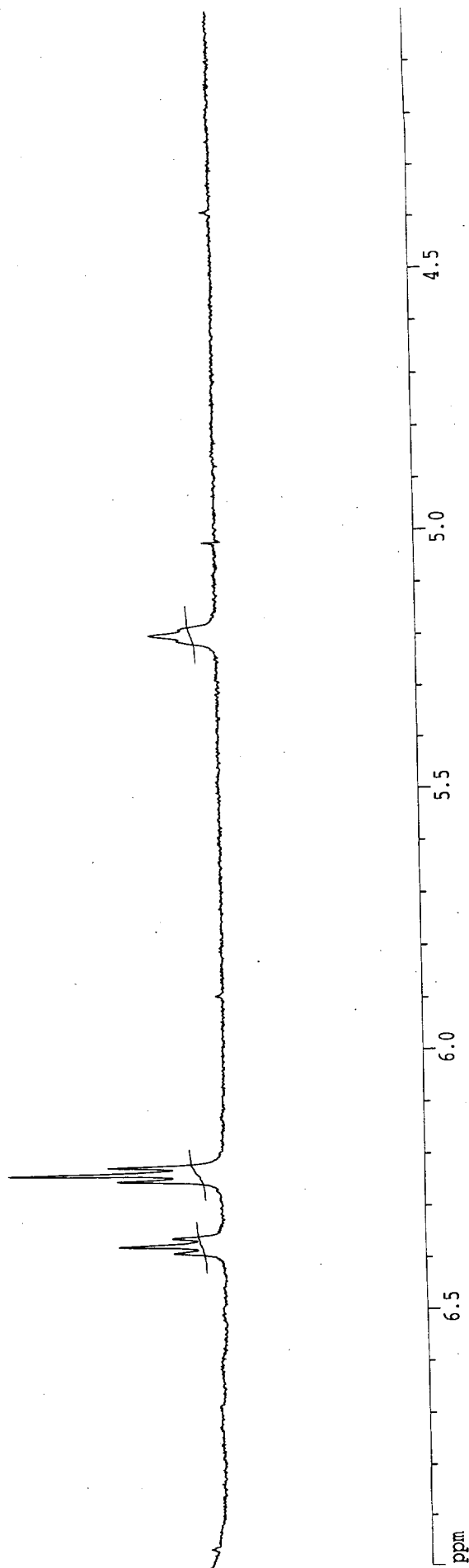


330 K
benzene- d_6

2 M = 2H, R = $n\text{-C}_{11}\text{H}_{23}$, $R^1 = n\text{-C}_7\text{H}_{15}$

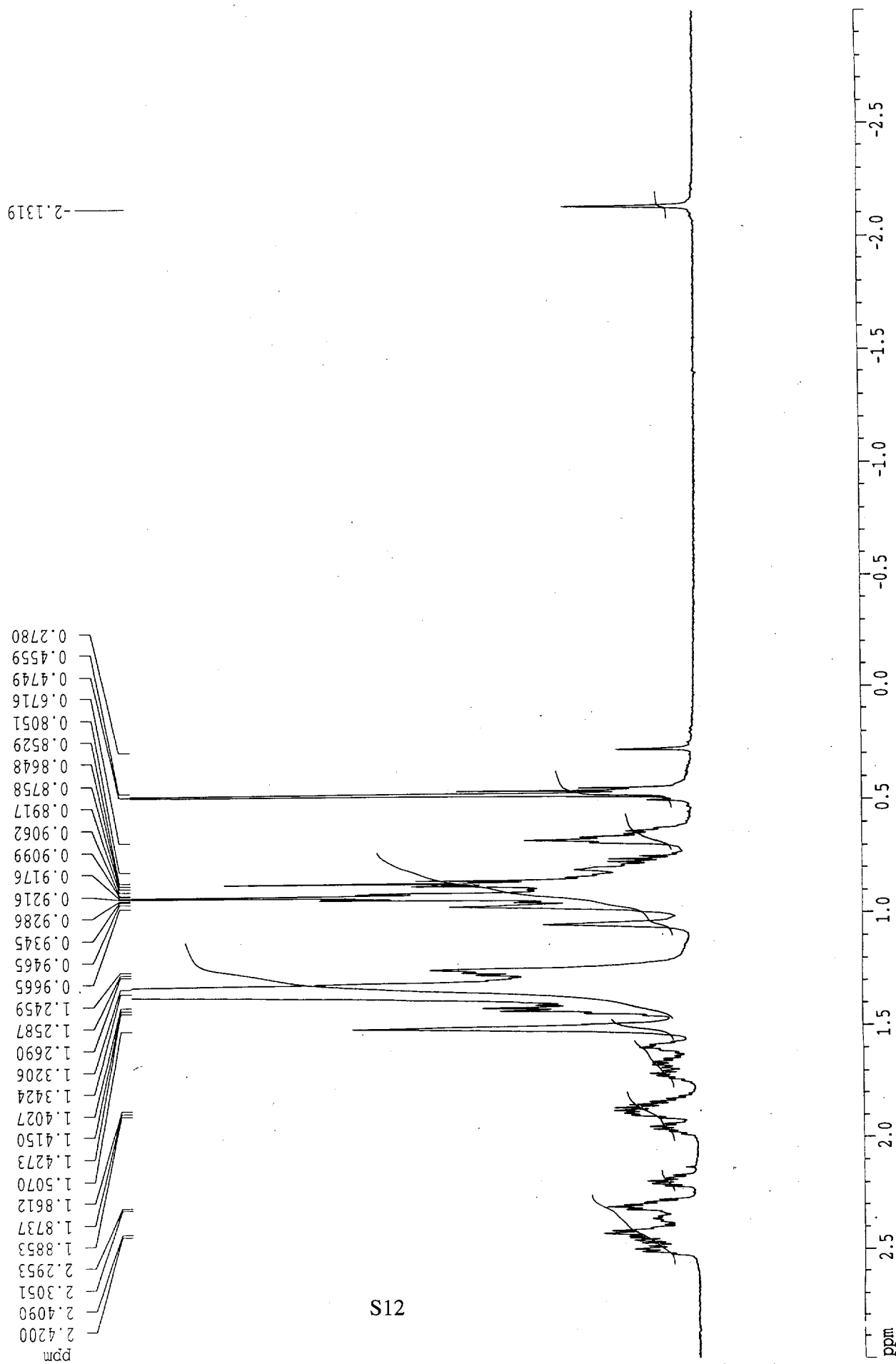
6.38603
6.37256
6.35872
6.24706
6.23357
6.21986

5.19661
5.02074



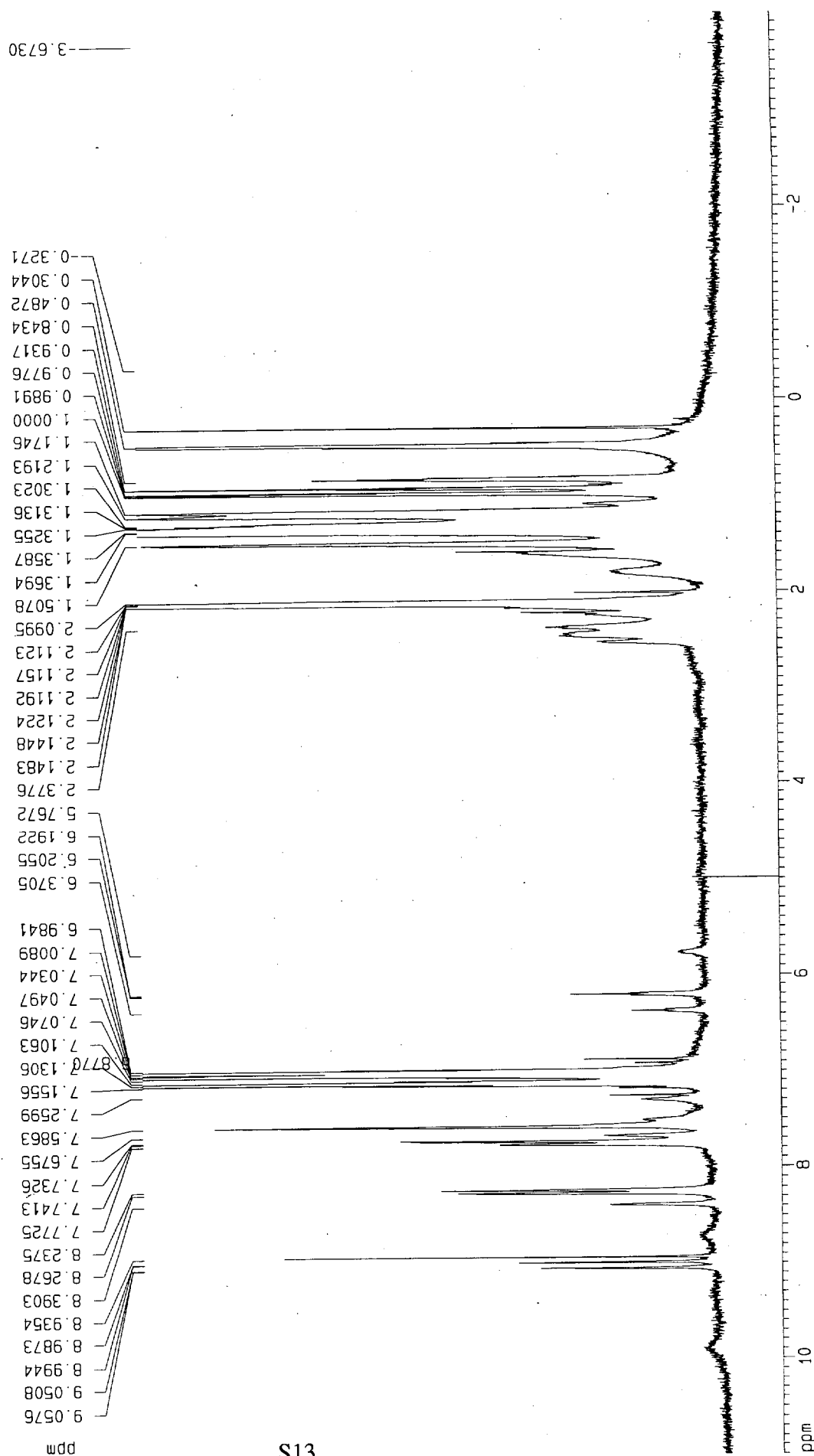
330 K
benzene- d_6

2 M = 2H, R = $n\text{-C}_{11}\text{H}_{23}$, R' = $n\text{-C}_7\text{H}_{15}$

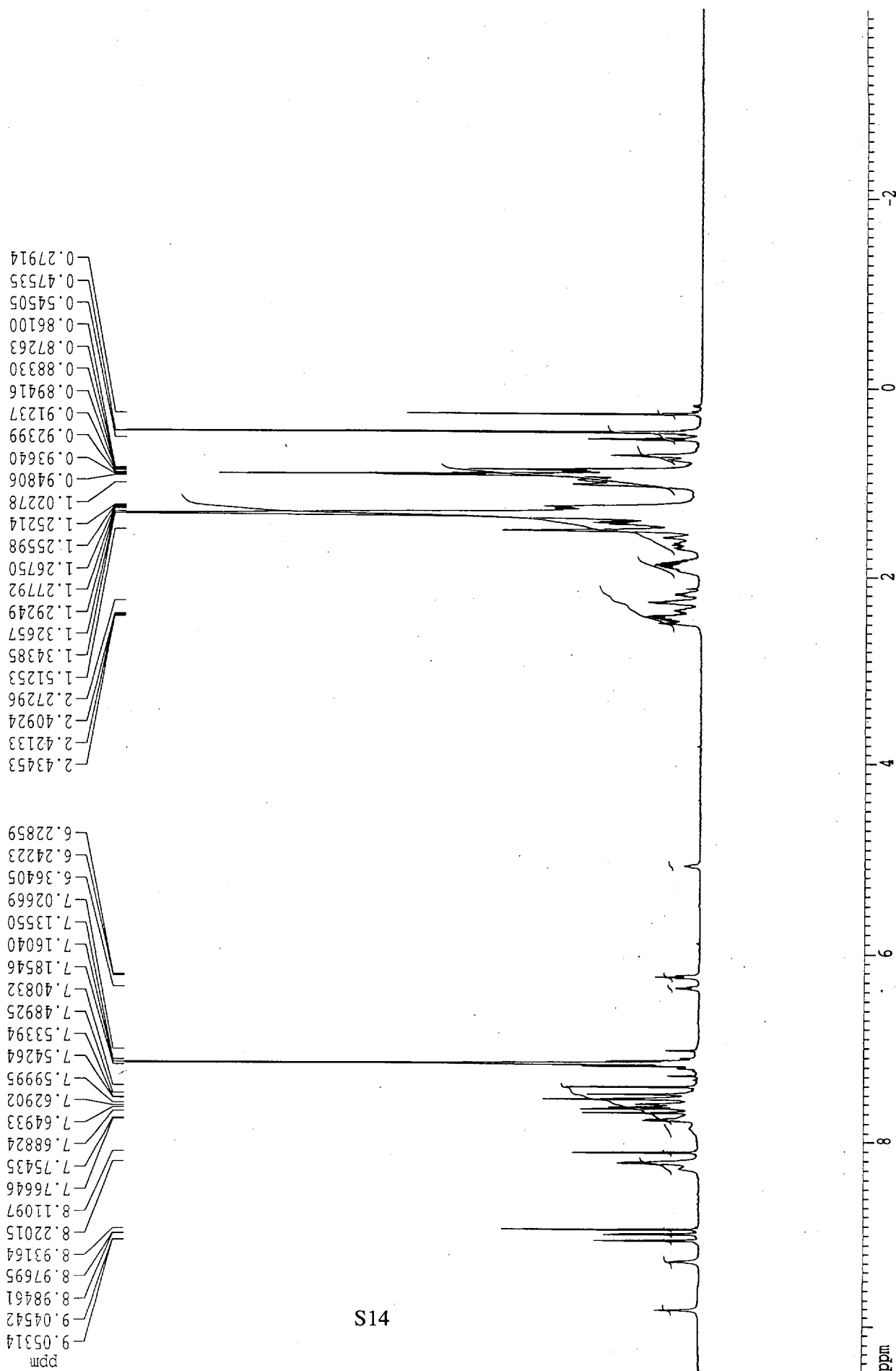


295 K
toluene-*d*₈

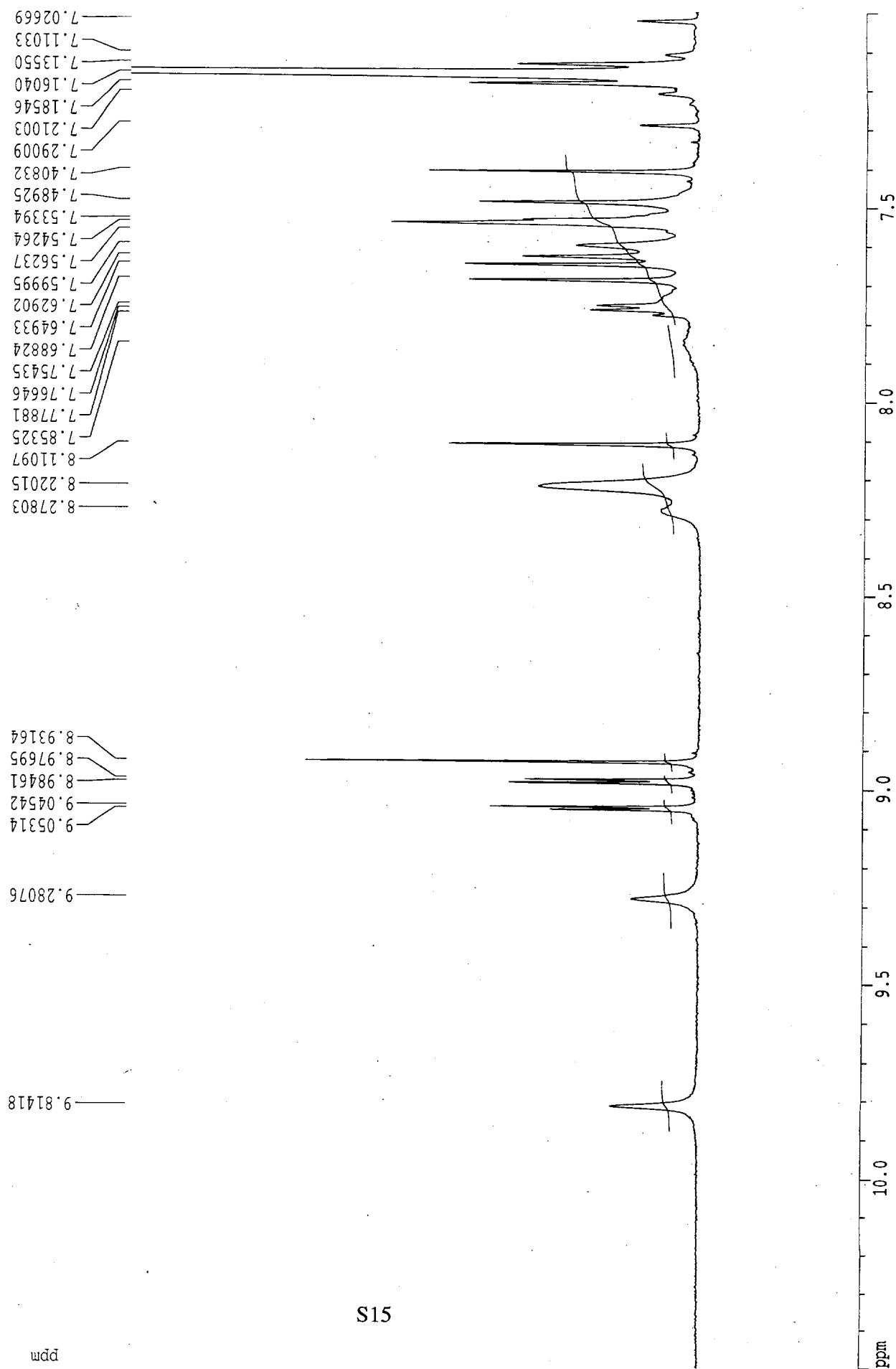
2 M = Zn, R = *n*-C₁₁H₂₃, R¹ = *n*-C₇H₁₅



2 M = Zn, R = $n\text{-C}_{11}\text{H}_{23}$, R' = $n\text{-C}_7\text{H}_{15}$ 330 K
benzene- d_6



2 M = Zn, R = $n\text{-C}_{11}\text{H}_{23}$, R' = $n\text{-C}_7\text{H}_{15}$
 330 K
 benzene- d_6



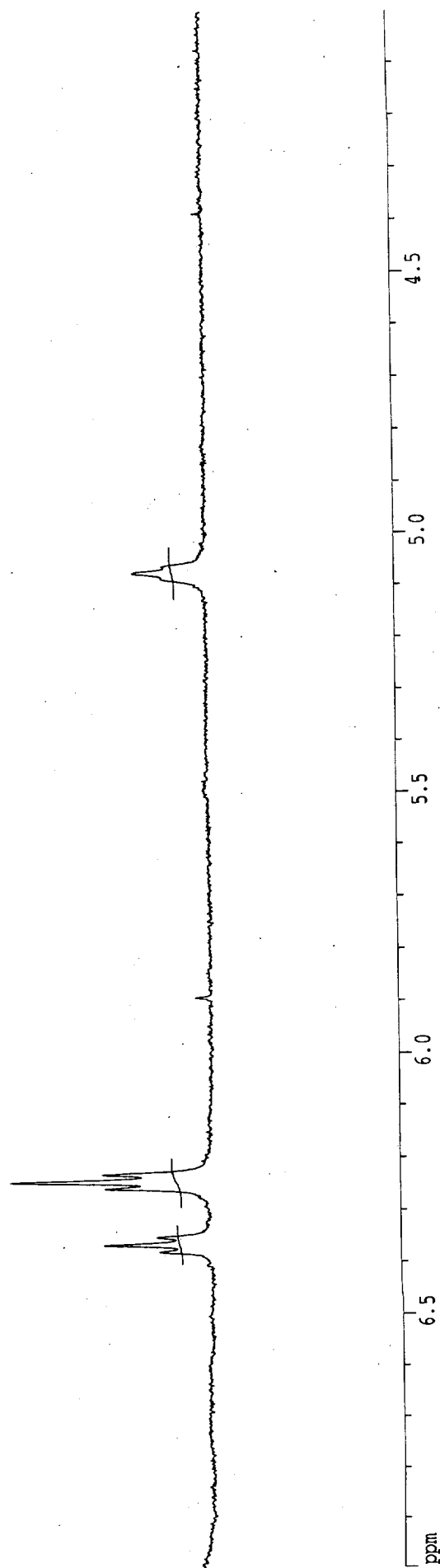
330 K
benzene-*d*₆

2 M = Zn, R = *n*-C₁₁H₂₃, R' = *n*-C₇H₁₅

6.37747
6.36405
6.35031
6.25564
6.24223
6.22859

5.07638

S16



330 K
benzene-*d*₆

2 M = Zn, R = *n*-C₁₁H₂₃, R' = *n*-C₇H₁₅

2.43453
2.42133
2.40924
2.27296
1.51253
1.43126
1.41861
1.34385
1.32657
1.29249
1.27792
1.26750
1.25598
1.25214
1.02278
0.98112
0.94806
0.93640
0.92399
0.91237
0.89416
0.88330
0.87263
0.86100
0.71193
0.55720
0.54505
0.47535
0.27914

ppm

S15

-3

-2

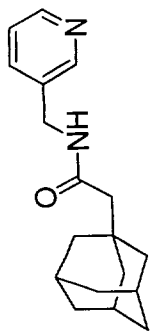
-1

0

1

2

ppm



9b

273 K
toluene-*d*₈

0.55932
1.50665
1.53676
1.55322
1.57288
1.60726
1.62739
1.87383
2.04862
2.05161
2.05568
2.05868
2.06287
2.07004

3.93453
3.92437

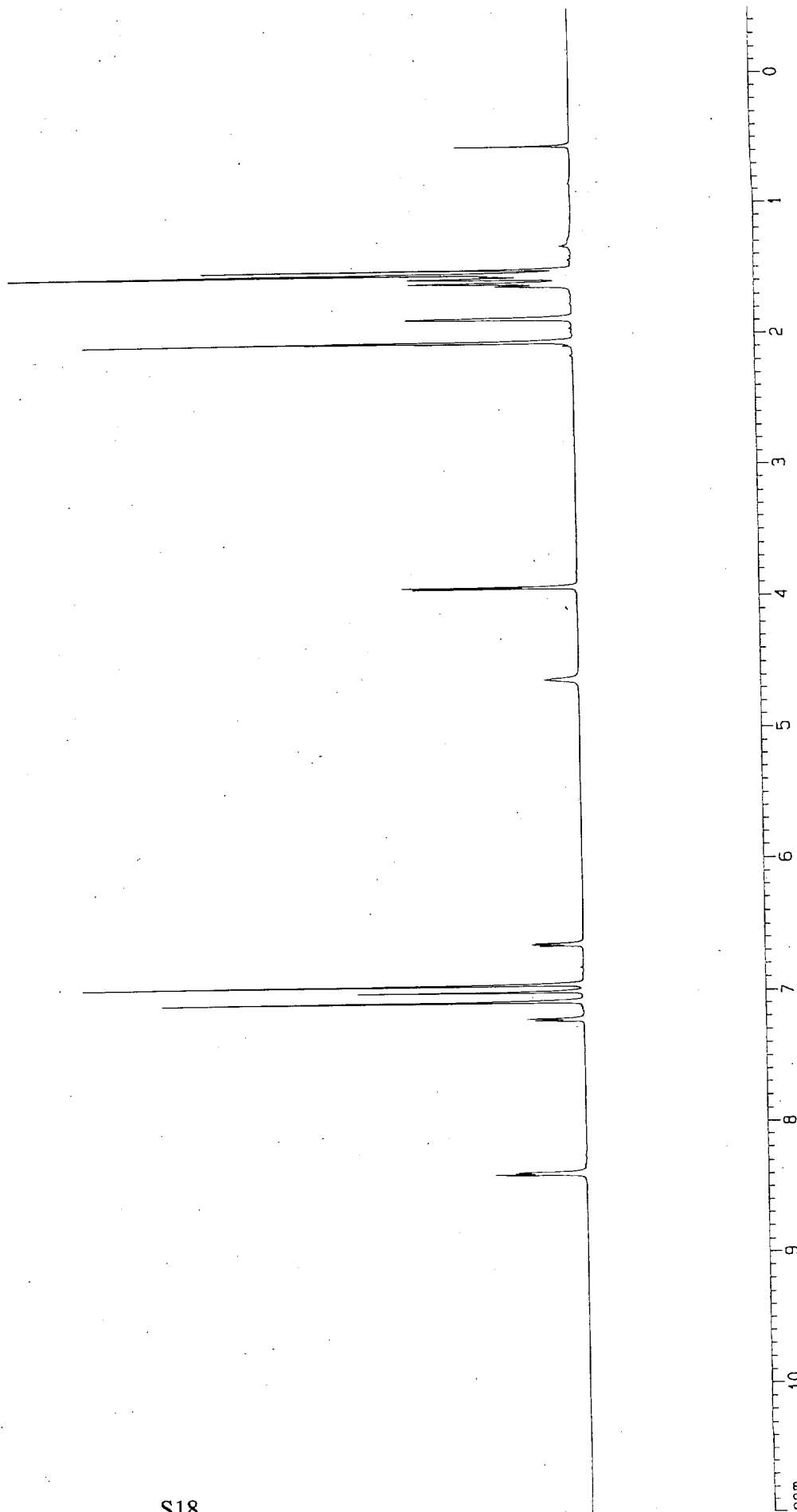
4.62307

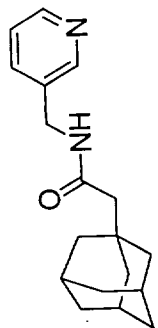
6.63324
6.64115
6.64609
6.65387
6.94970
7.00107
7.08105
7.21130
7.22396

8.37463
8.38138
8.39112

ppm

S18

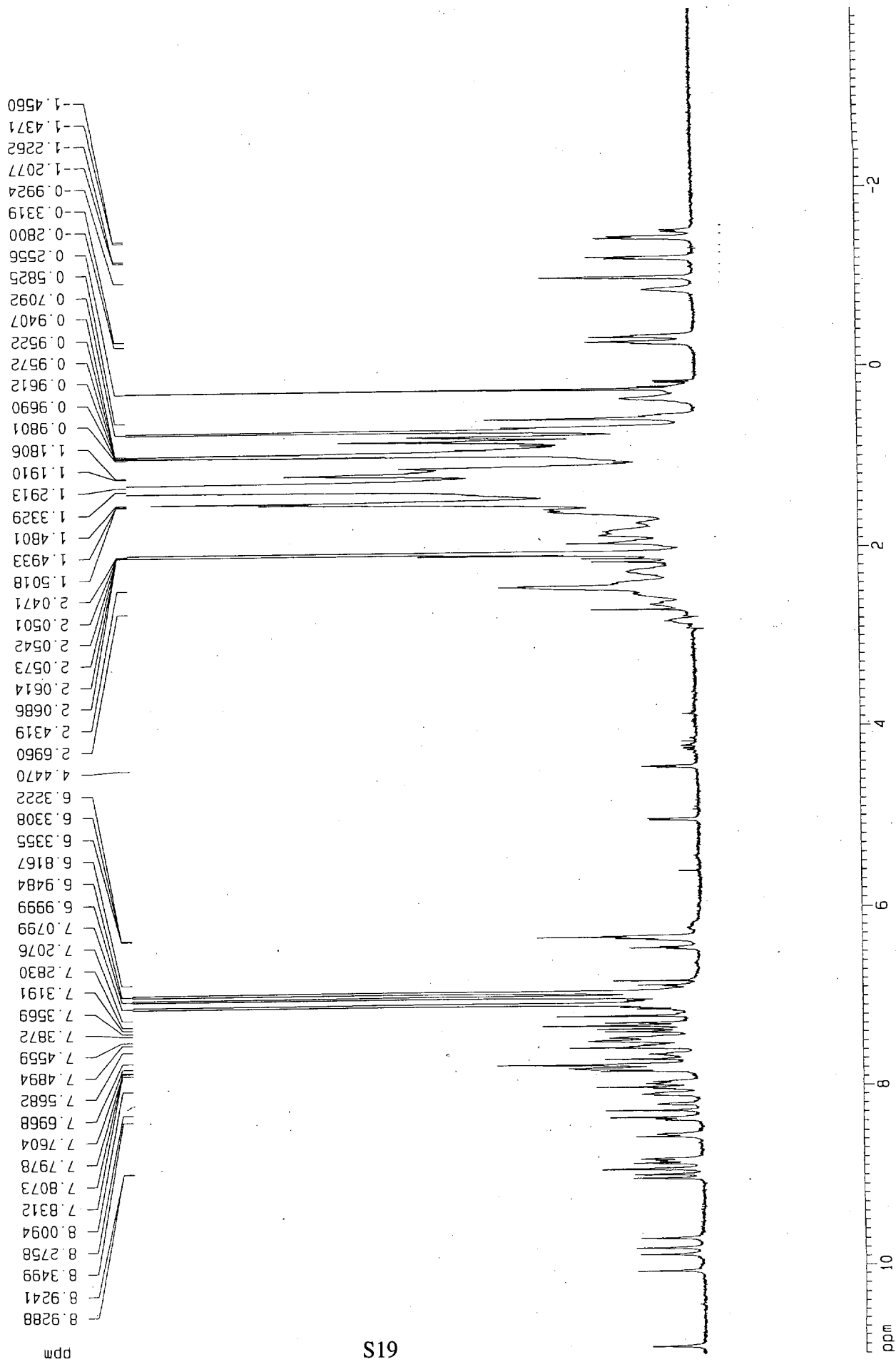


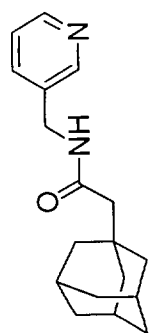
273 K
toluene- d_8

+

$$2 \text{ M} = \text{Zn}, \text{ R} = n\text{-C}_{11}\text{H}_{23}, \text{ R}^1 = n\text{-C}_7\text{H}_{15}$$

9b 1 equivalent

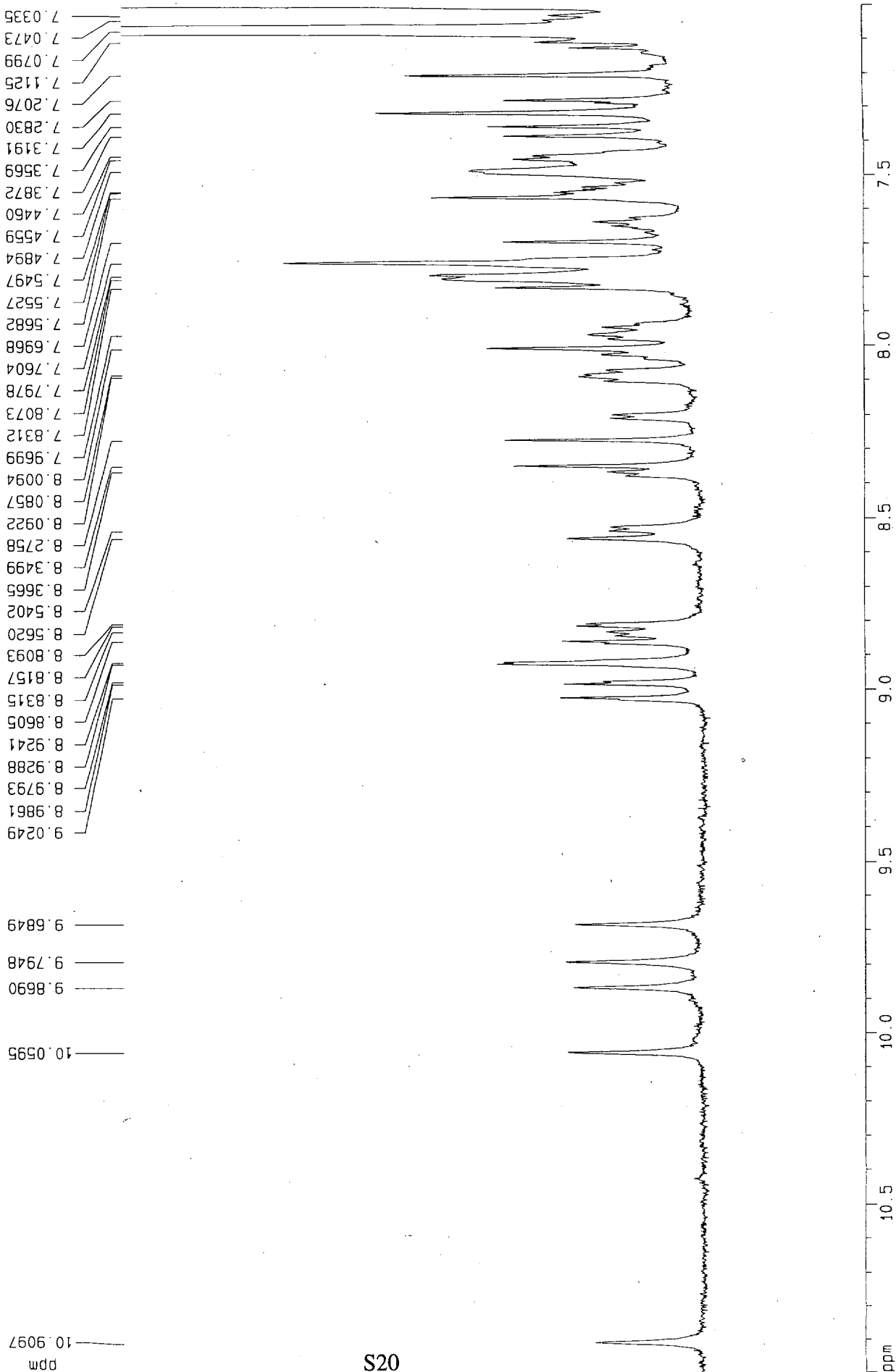


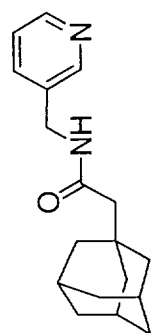


273 K
toluene-*d*₈

9b 1 equivalent

2 M = Zn, R = *n*-C₁₁H₂₃, R¹ = *n*-C₇H₁₅ +

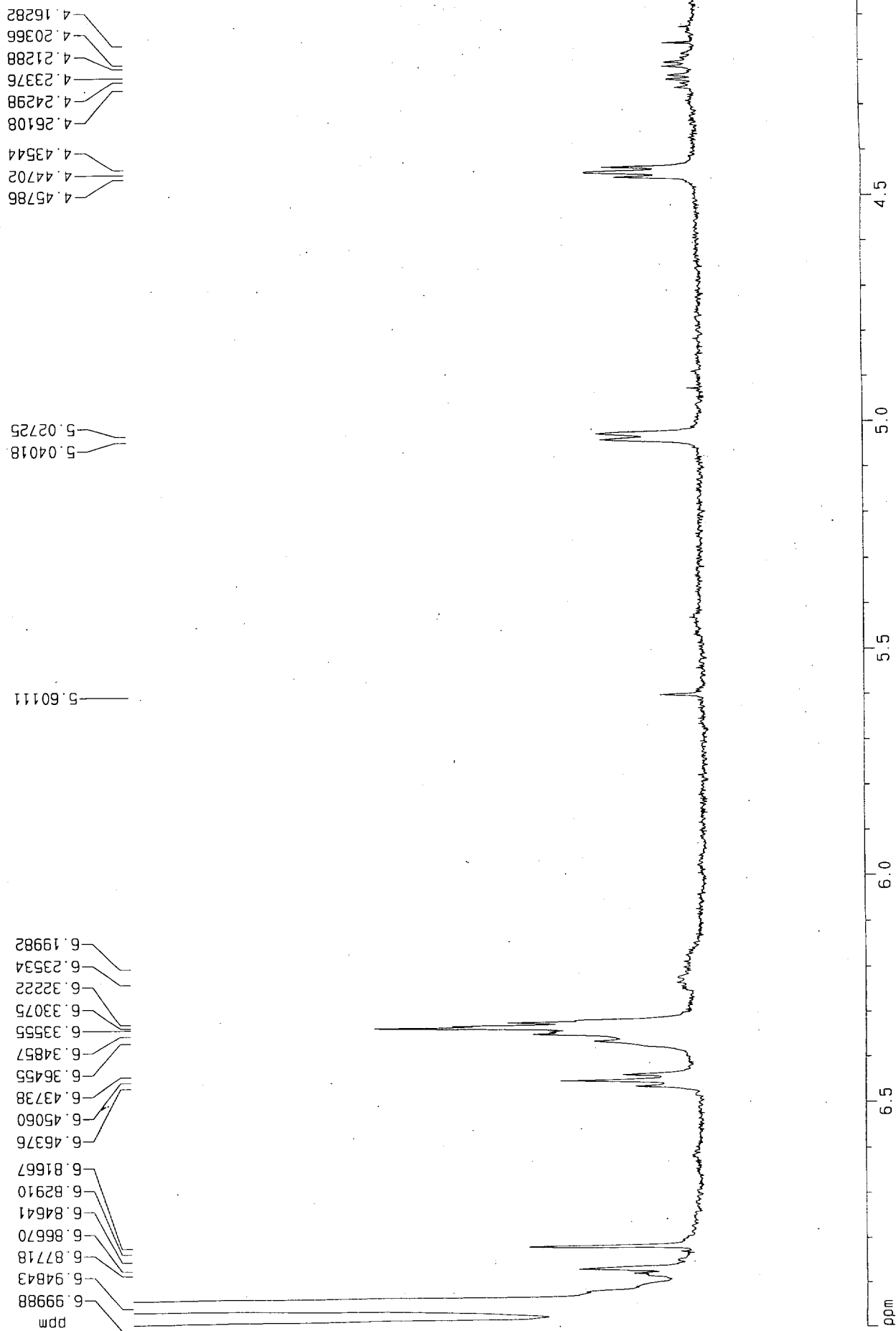




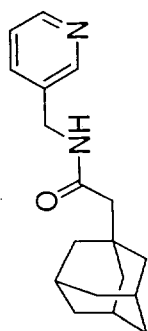
9b 1 equivalent

273 K
toluene-*d*₈

2 M = Zn, R = *n*-C₁₁H₂₃, R¹ = *n*-C₇H₁₅

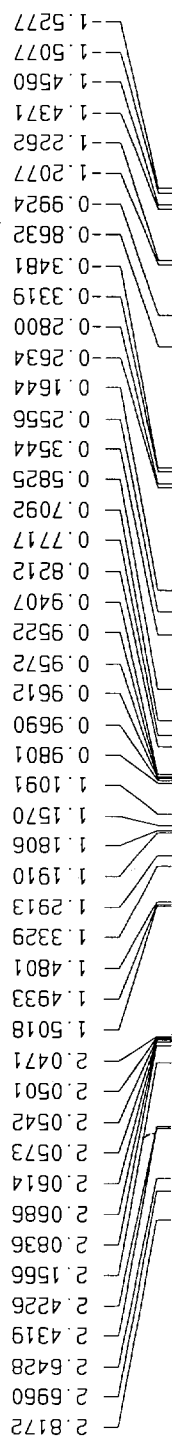


273 K
toluene-*d*₈

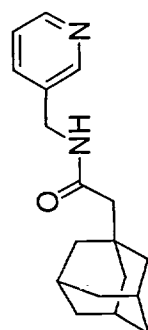


9b 1 equivalent

2 M = Zn, R = *n*-C₁₁H₂₃, R¹ = *n*-C₇H₁₅ +

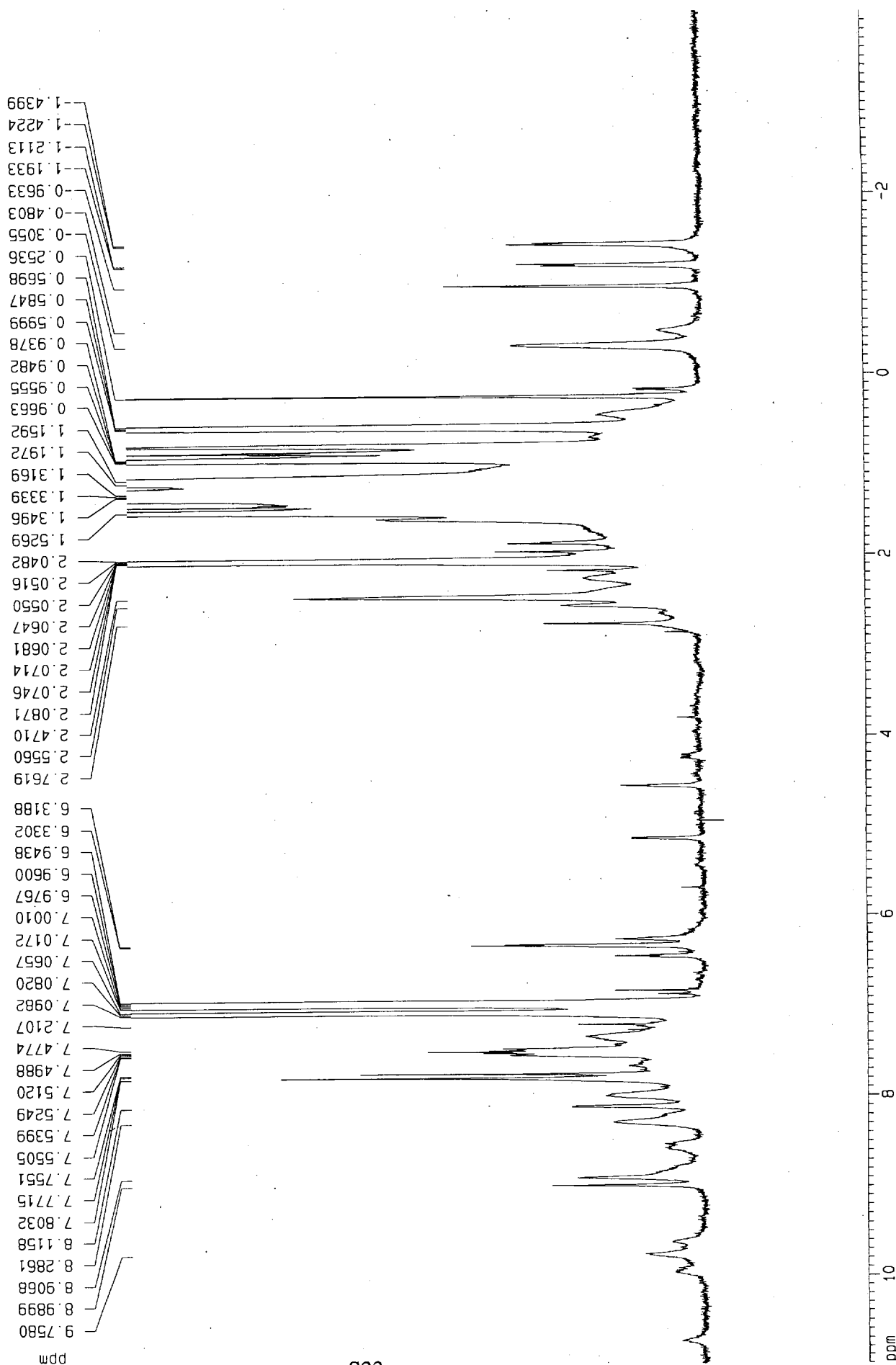


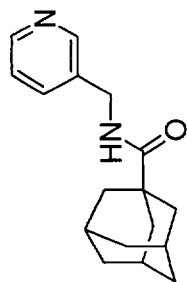
295 K
toluene-*d*₈



9b 1 equivalent

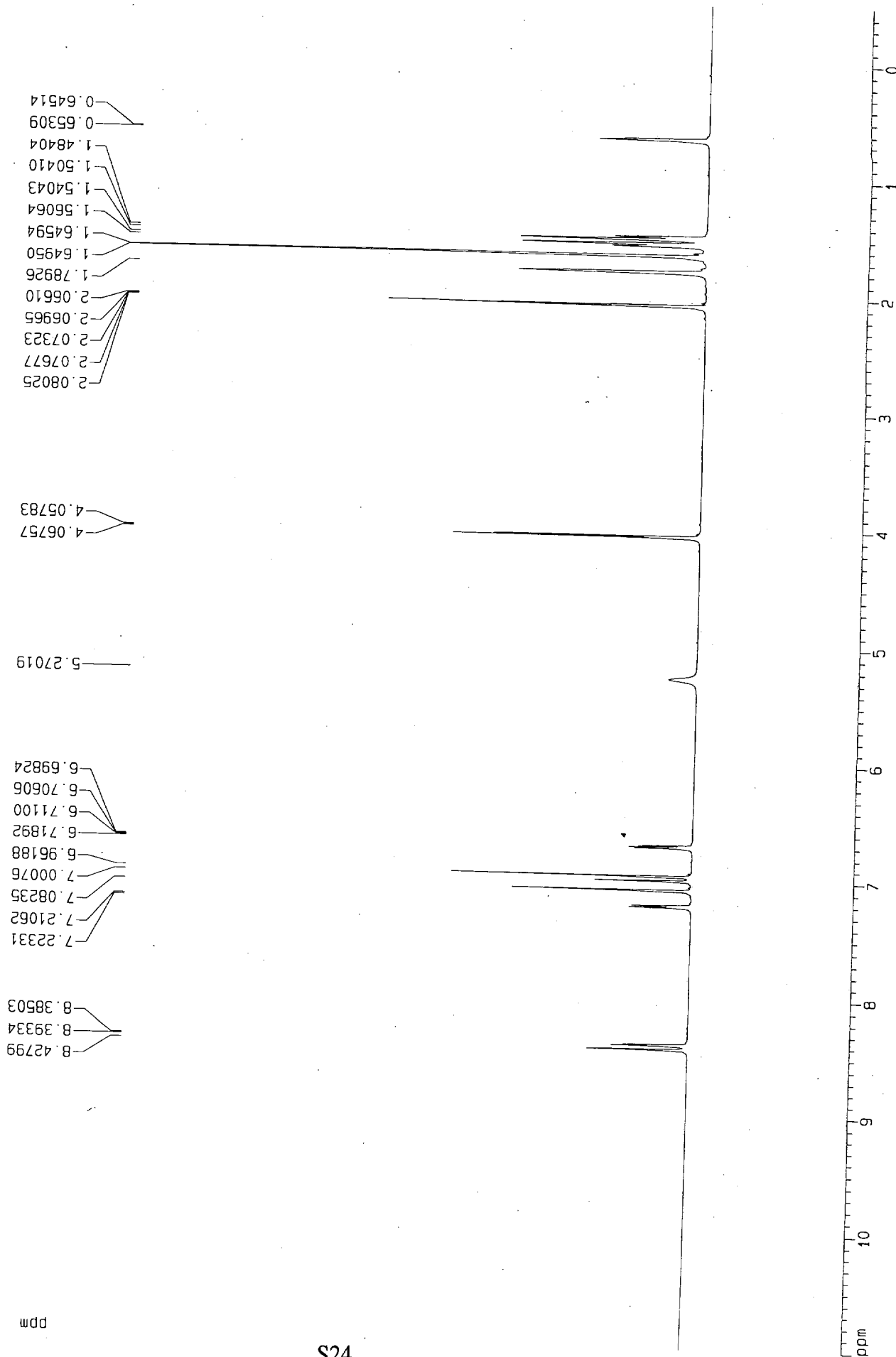
2 M = Zn, R = *n*-C₁₁H₂₃, R¹ = *n*-C₇H₁₅ +

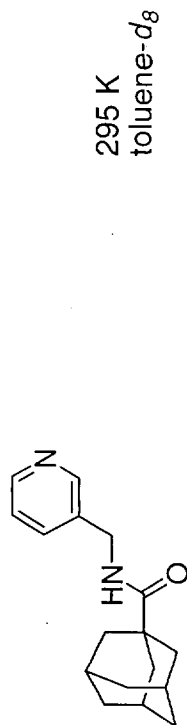




295 K
toluene-*d*₈

9a

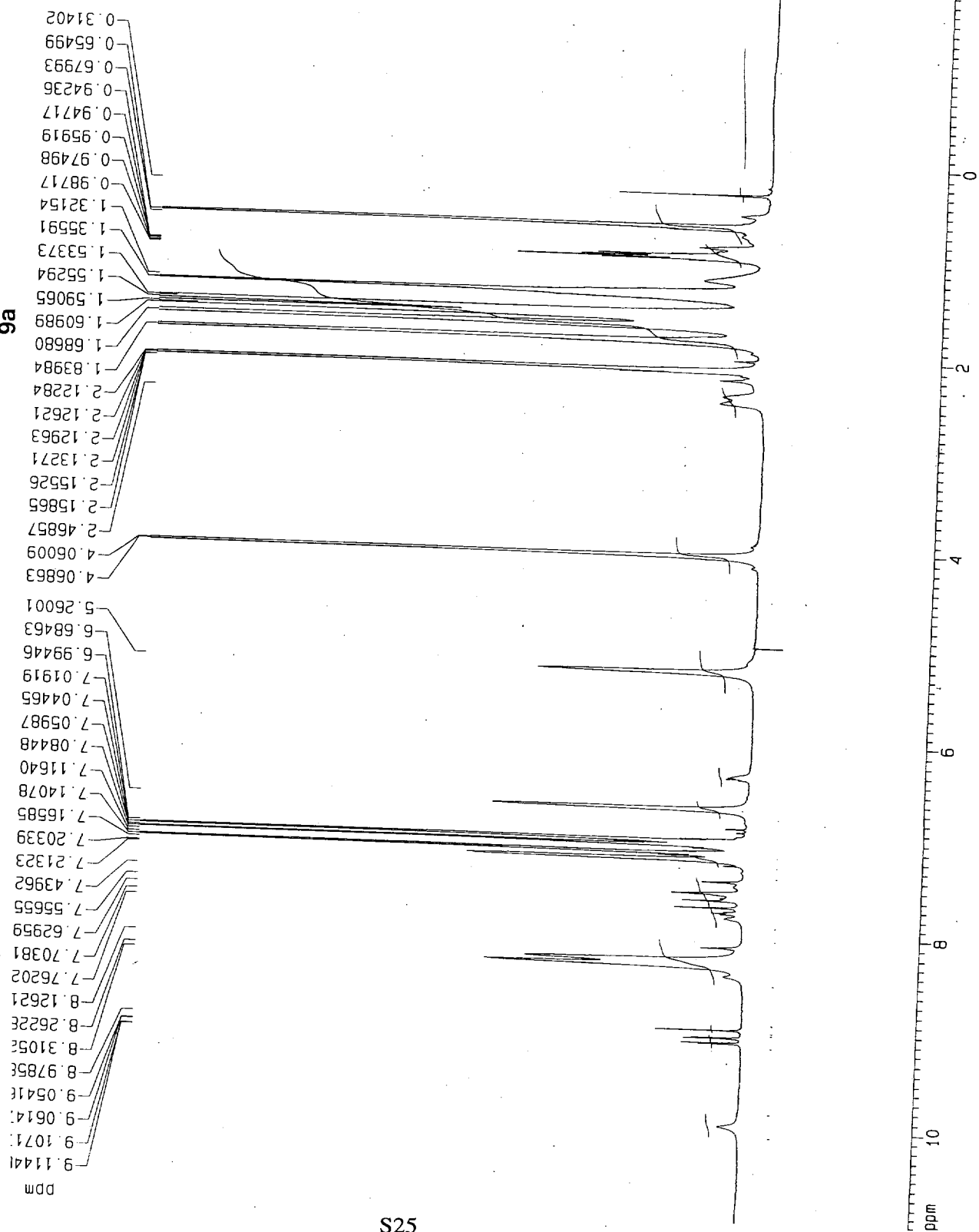




295 K
toluene- d_8

large excess

9a



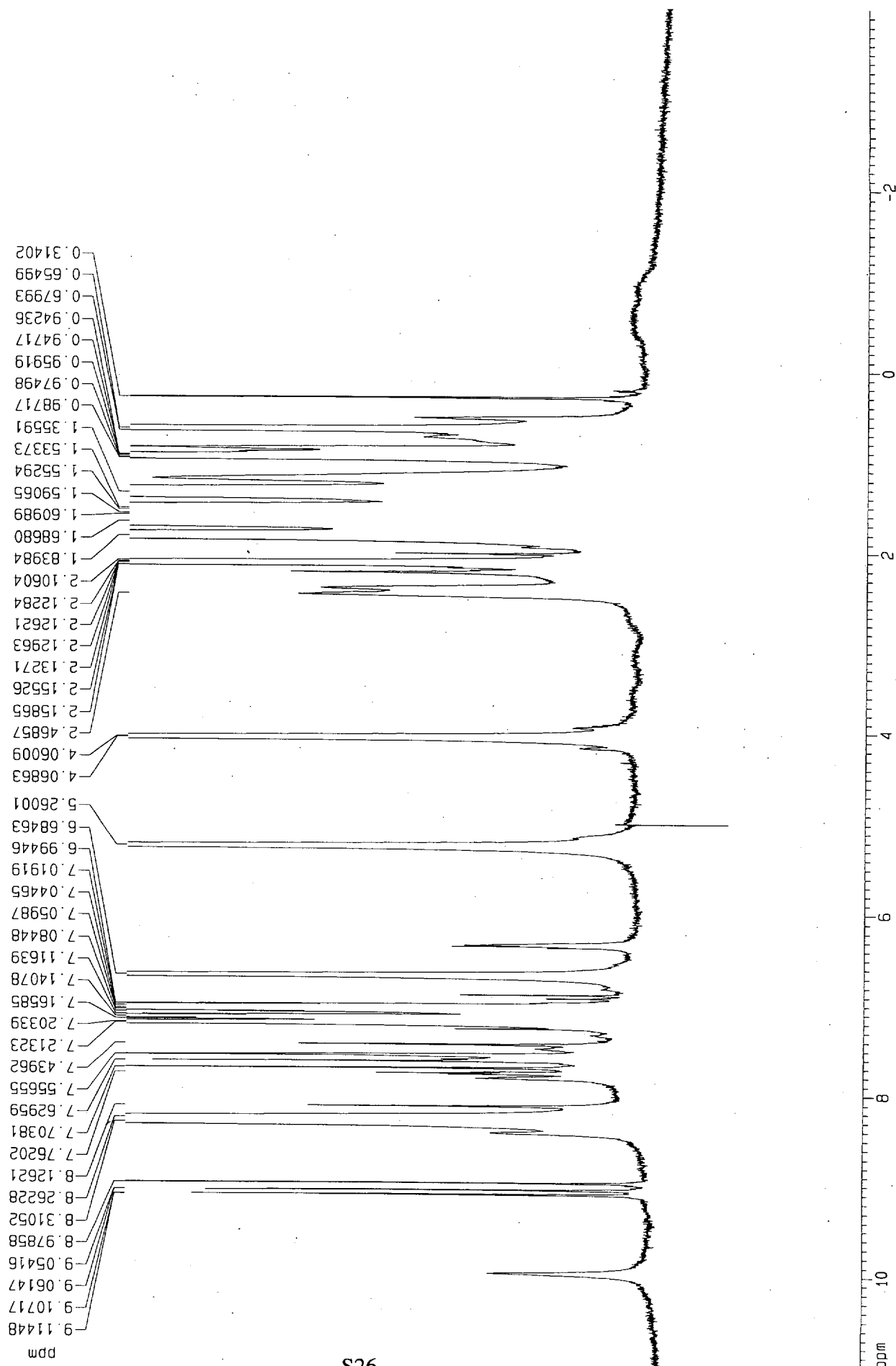


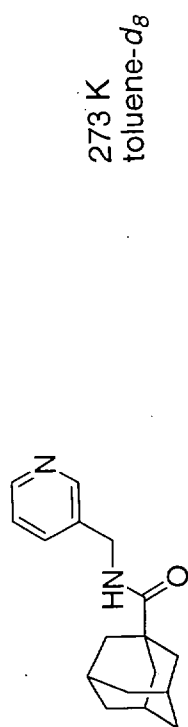
295 K
toluene- d_8

$$2 \text{ M} = \text{Zn}, \text{ R} = n\text{-C}_{11}\text{H}_{23}, \text{ R}^1 = n\text{-C}_7\text{H}_{15}$$

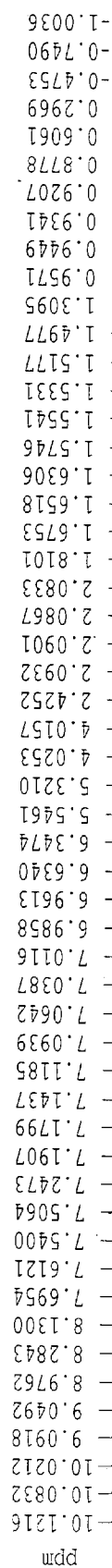
large excess

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large excess



S27

