ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Novel dansyl-appended calix[4]arene frameworks: fluorescence properties and mercury sensing

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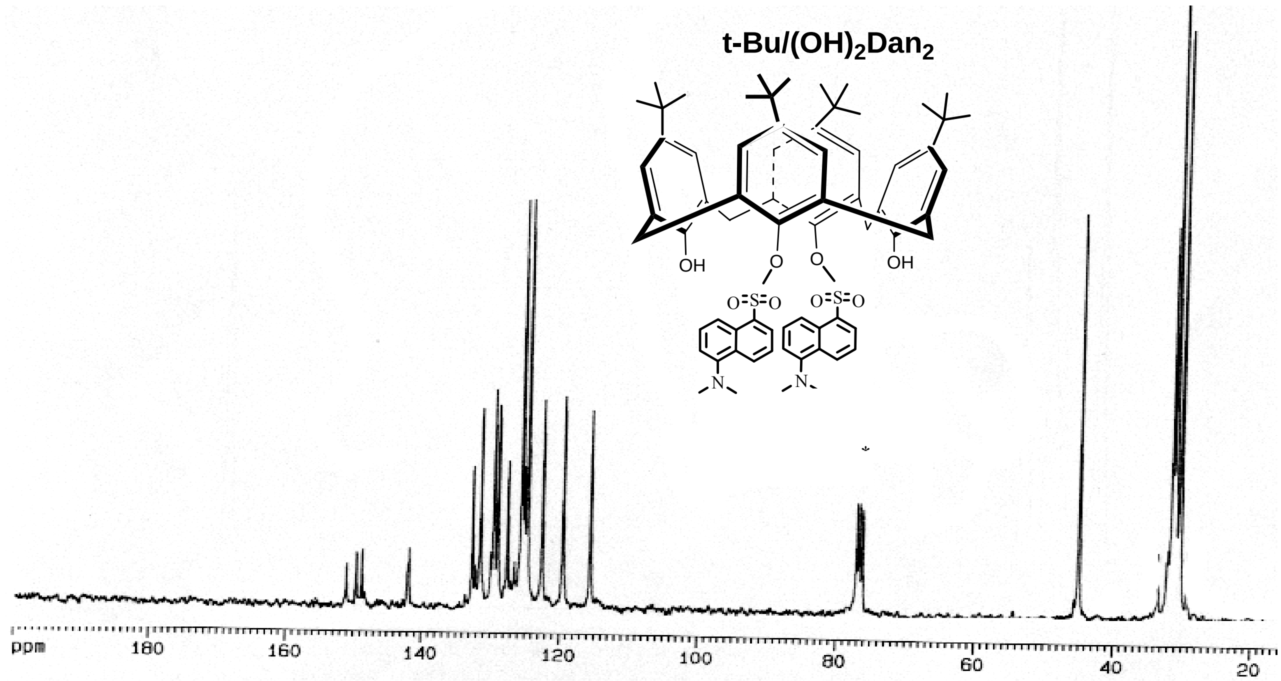


Figure S1. ^{13}C NMR spectra of **t-Bu/(OH)$_2$Dan$_2$** in $CDCl_3$ at 25°C. (*) represents signal due to residual solvents.

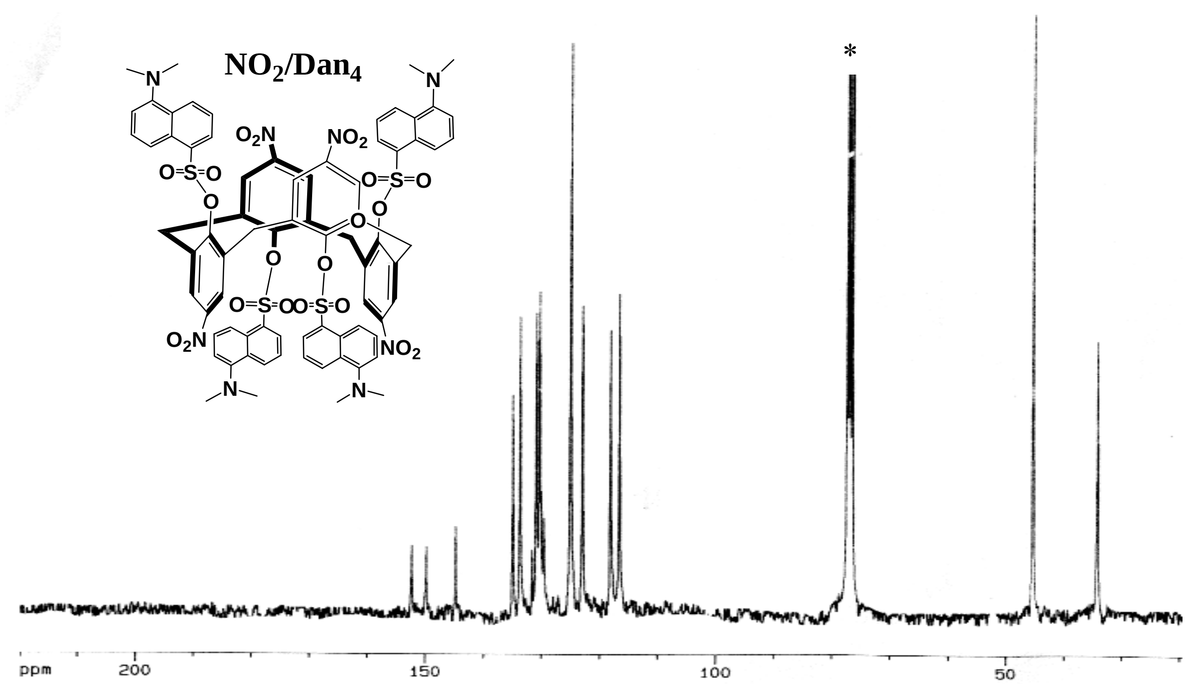


Figure S2. ^{13}C NMR spectra of **NO$_2$/Dan$_4$** in $CDCl_3$ at 25°C. (*) represents signal due to residual solvents.

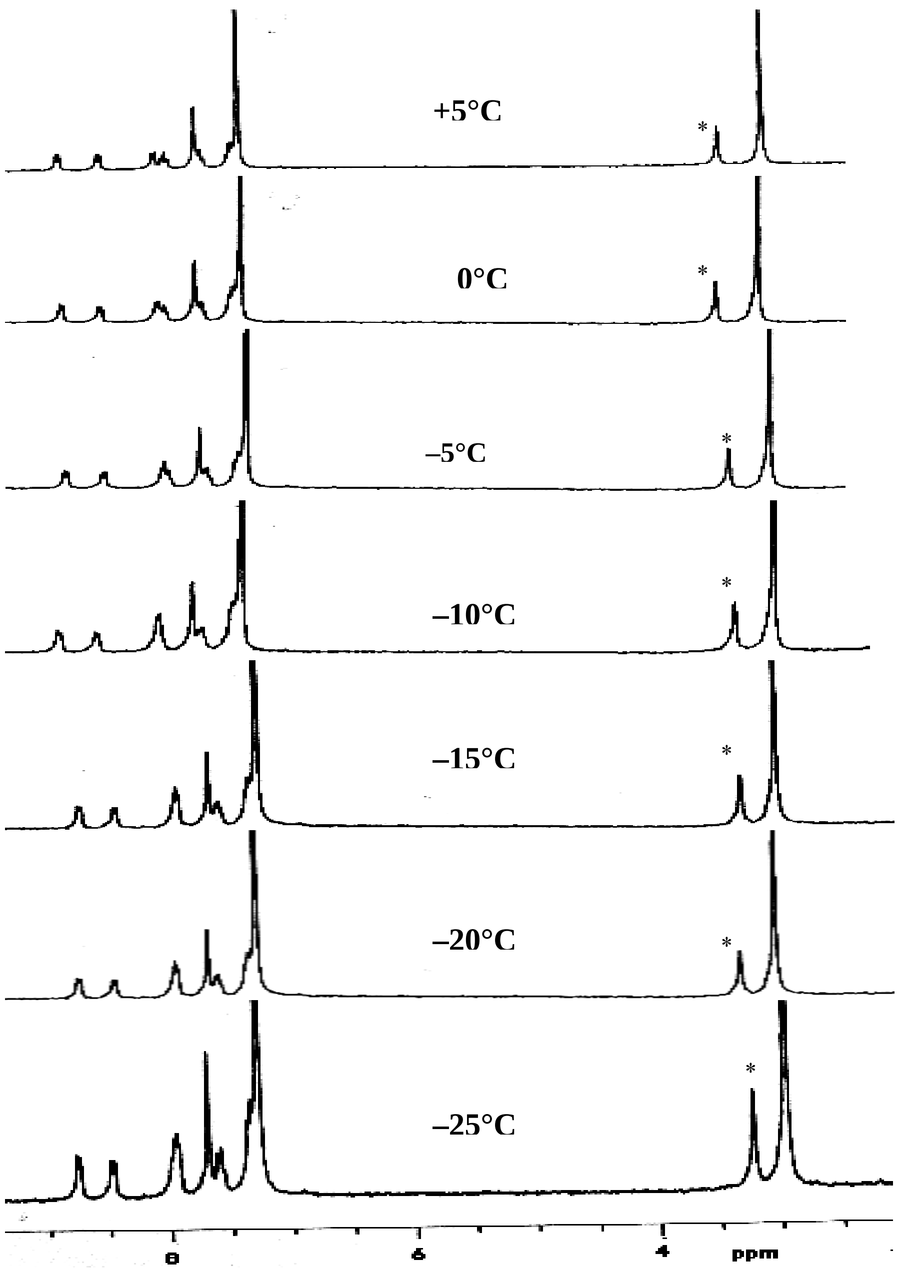


Figure S3. Temperature-dependent partial [1]H NMR spectra of $\mathbf{NO_2/Dan_4}$ in $CDCl_3$ showing singlet of methylene-bridged protons (peak labeled as *).

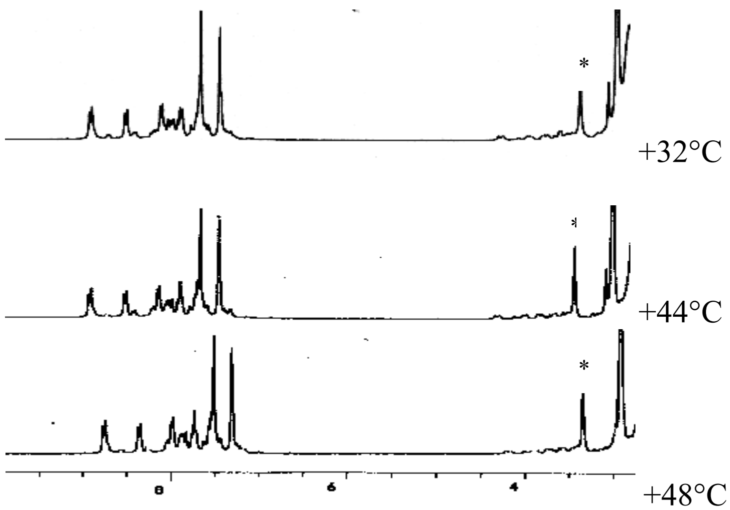


Figure S4. ^{1}H NMR spectra of **NO_2/Dan$_4$** in $CDCl_3$ at high temperatures. * represents singlet for the methylene-bridged protons.

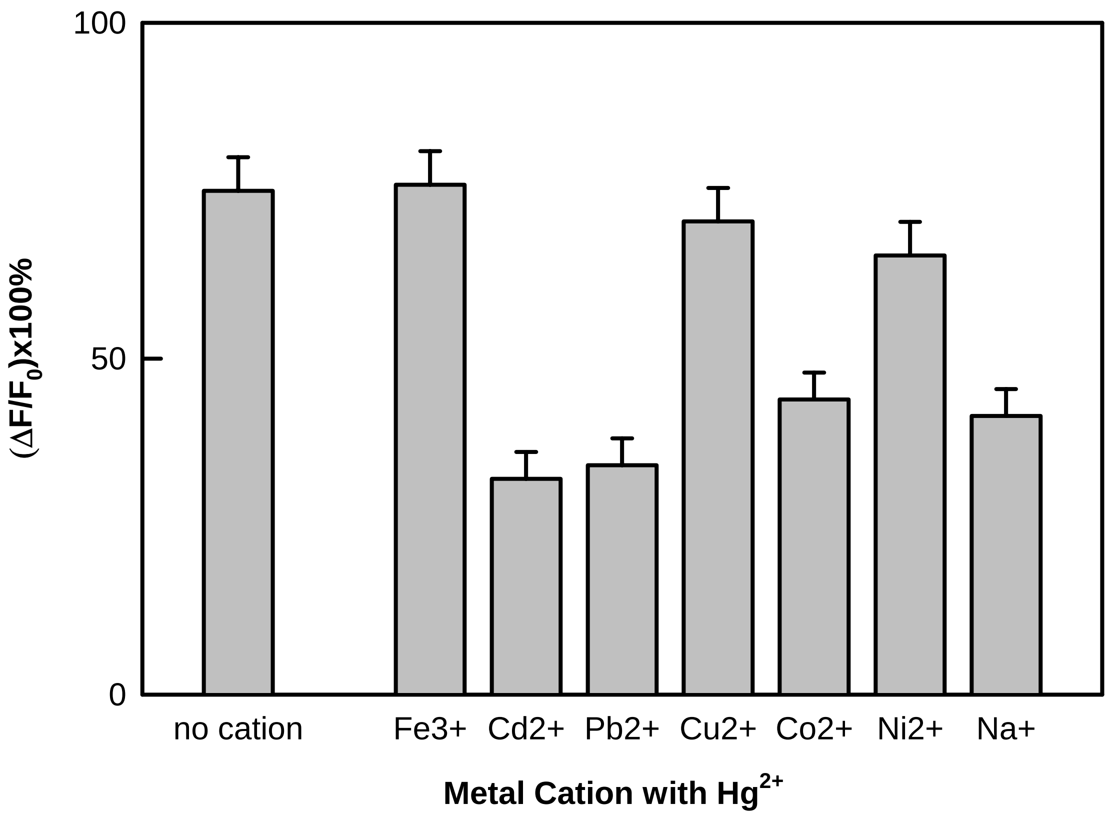


Figure S5. % reduction in the fluorescence intensity of **NO_2/Dan$_4$** (1×10^{-5} M) in the presence of 8 μM each of M^{n+} and Hg^{2+} in acetonitrile at ambient conditions ($\lambda_{excitation}$ = 351 nm).

Calculation of Equilibrium Constant (K_{eq}).

$$2NO_2/Dan_4 + Hg^{2+} \xleftrightarrow{K_{eq}} (NO_2/Dan_4)_2Hg^{2+}$$

@ t = 0 $\quad [NO_2/Dan_4]_0 \; [Hg^{2+}]_0 \qquad 0$

@ t $_{eq}$ $\quad ([NO_2/Dan_4]_0 - 2x) \;\; ([Hg^{2+}]_0 - x) \qquad x$

where,

$$K_{eq} = \frac{[(NO_2/Dan_4)_2Hg^{2+}]_{eq}}{[NO_2/Dan_4]_{eq}^2[Hg^{2+}]_{eq}}$$

$$K_{eq} = \frac{x}{([NO_2/Dan_4]_0 - 2x)^2([Hg^{2+}]_0 - x)}$$

Now, assuming

$$[(NO_2/Dan_4)_2Hg^{2+}]_{eq} = x = a_1\Delta F$$

and

$$[(NO_2/Dan_4)_2]_{eq} = ([NO_2/Dan_4]_0 - 2x) = a_2F$$

where ΔF and F are the decrease in fluorescence intensity and the fluorescence intensity at the wavelength of analysis, respectively; and a_1 and a_2 are the corresponding proportionality constants. Now,

$$K_{eq} = \frac{a_1\Delta F}{a_2^2F^2([Hg^{2+}]_0 - a_1\Delta F)}$$

which rearranges to

$$\frac{1}{F^2} = \left(\frac{K_{eq}a_2^2}{a_1}\right)\frac{[Hg^{2+}]_0}{\Delta F} - K_{eq}a_2^2$$

A plot of $\frac{1}{F^2}$ *versus* $\frac{[Hg^{2+}]_0}{\Delta F}$ should be linear with slope = $\frac{K_{eq}a_2^2}{a_1}$ and *y*-intercept = $K_{eq}a_2^2$.

From y-intercept and knowledge of a_2, K_{eq} is assessed. The parameter a_2 was obtained separately from a linear calibration analysis of $[NO_2 / Dan_4]$ *versus* F, which provides:

$[NO_2 / Dan_4] = 2.7(\pm 0.1)\times 10^{-6} F$; $r^2 = 0.9996$.

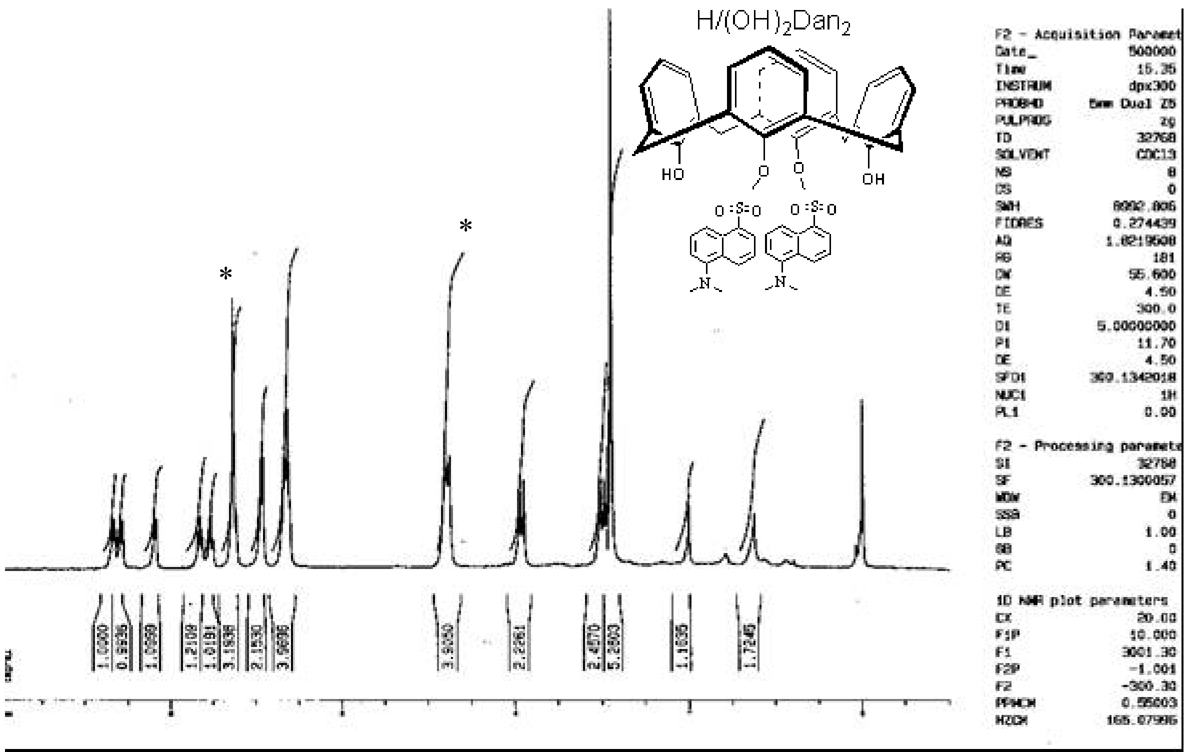
Similarly, linear regression analysis of $\frac{1}{F^2}$ *versus* $\frac{[Hg^{2+}]_0}{\Delta F}$ provides following expression:

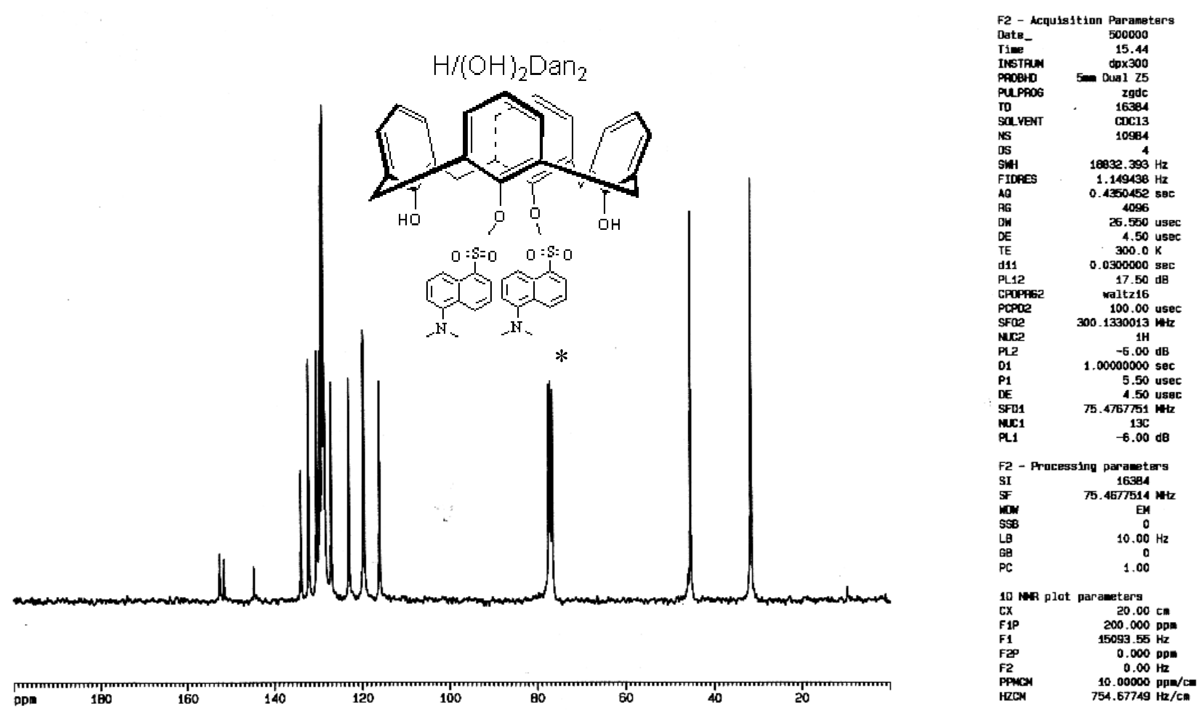
$$\frac{1}{F^2} = 1.6(\pm 0.2)\times 10^5 \frac{[Hg^{2+}]_0}{\Delta F} - 0.38(\pm 0.10)\,;\; r^2 = 0.9903$$

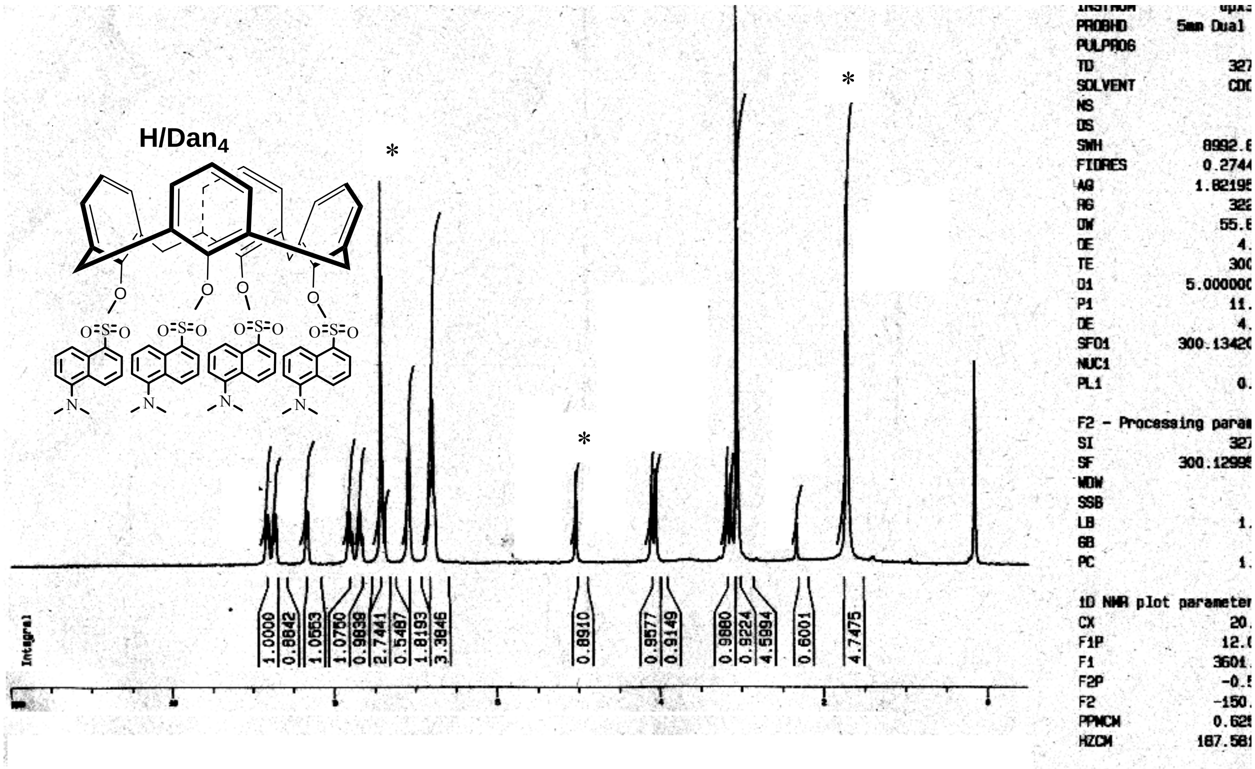
From, y-intercept = $K_{eq} a_2^2 = 0.38(\pm 0.10)$ and $a_2 = 2.7(\pm 0.1)\times 10^{-6}$ M;

$K_{eq} = 5.2(\pm 0.8)\times 10^{10}$ M^{-2}

$^1H/^{13}C$ NMR spectra of $H/(OH)_2Dan_2$, H/Dan_4, t-Bu/$(Ester)_2Dan_2$, H/$(Ester)_2Dan_2$, t-Bu/Dan_1, and NO_2/Dan_1. (*) represents signal due to residual solvents.



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0.9577
0.9149
0.9880
0.9224
4.5994
0.6001
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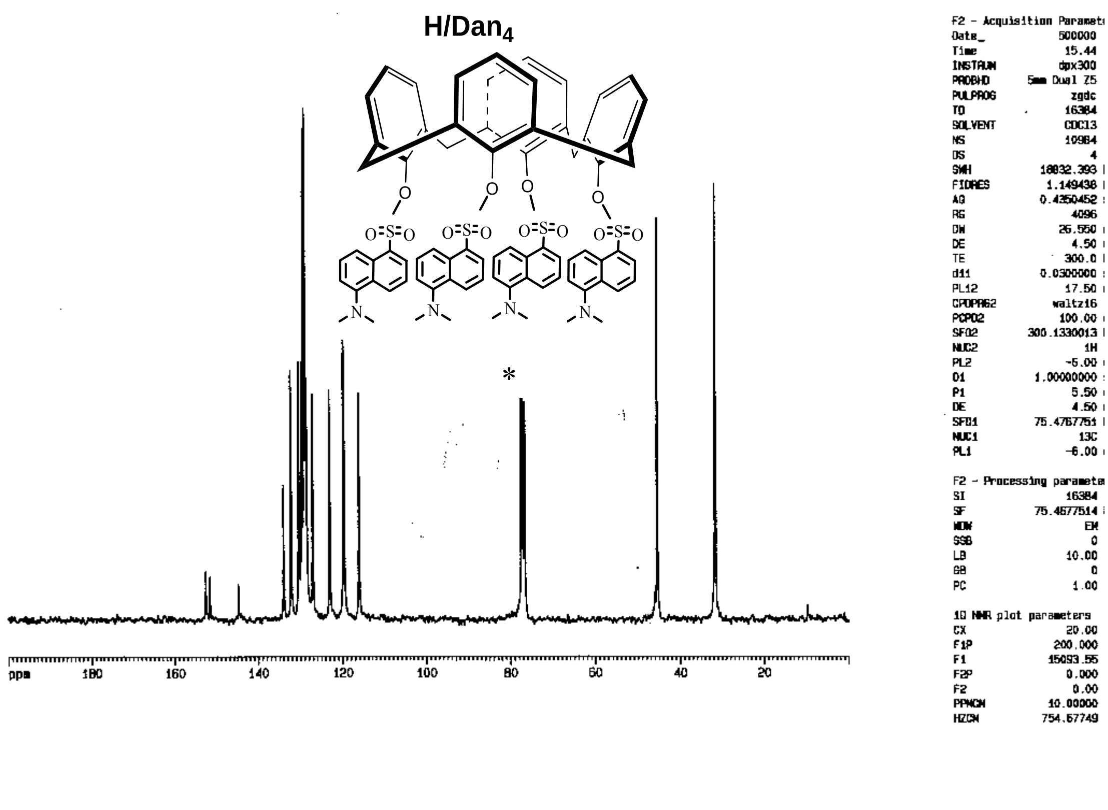
1D NMR plot parameter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F2 - Processing paramete
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SF 75.4677514
WDW EM
LB 10.00
1D NMR plot parameters
CX 20.00
F1P 200.000
F1 15093.55
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60
40
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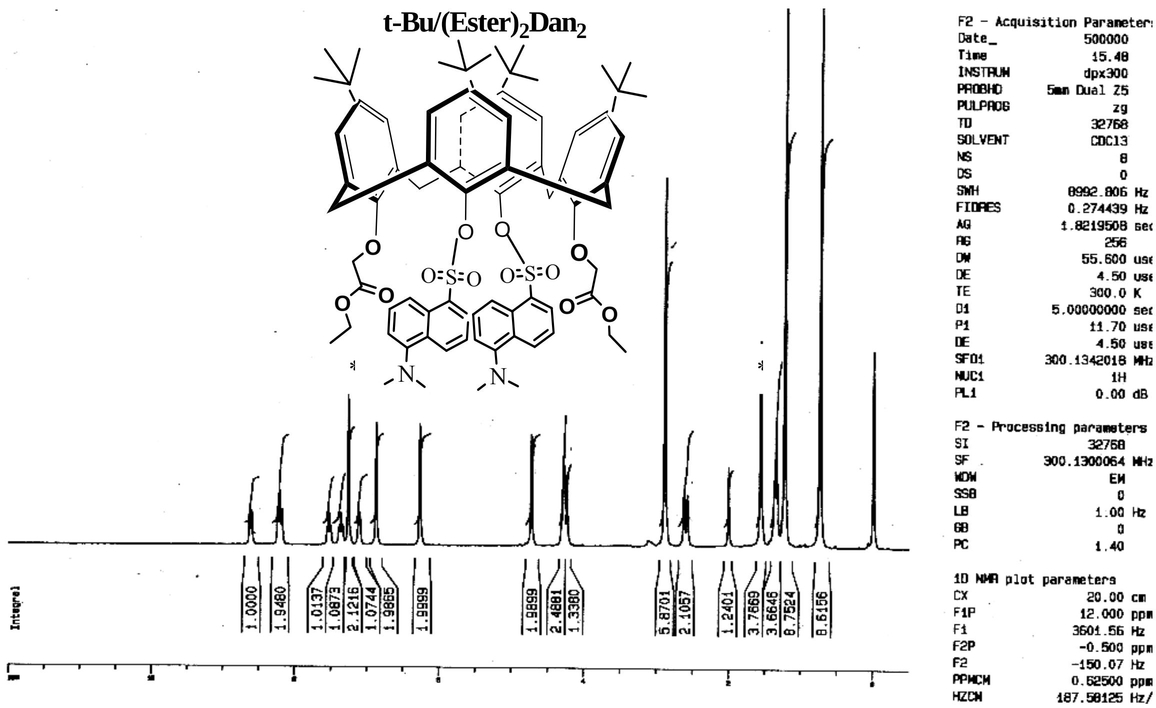
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O=S=O
N
N
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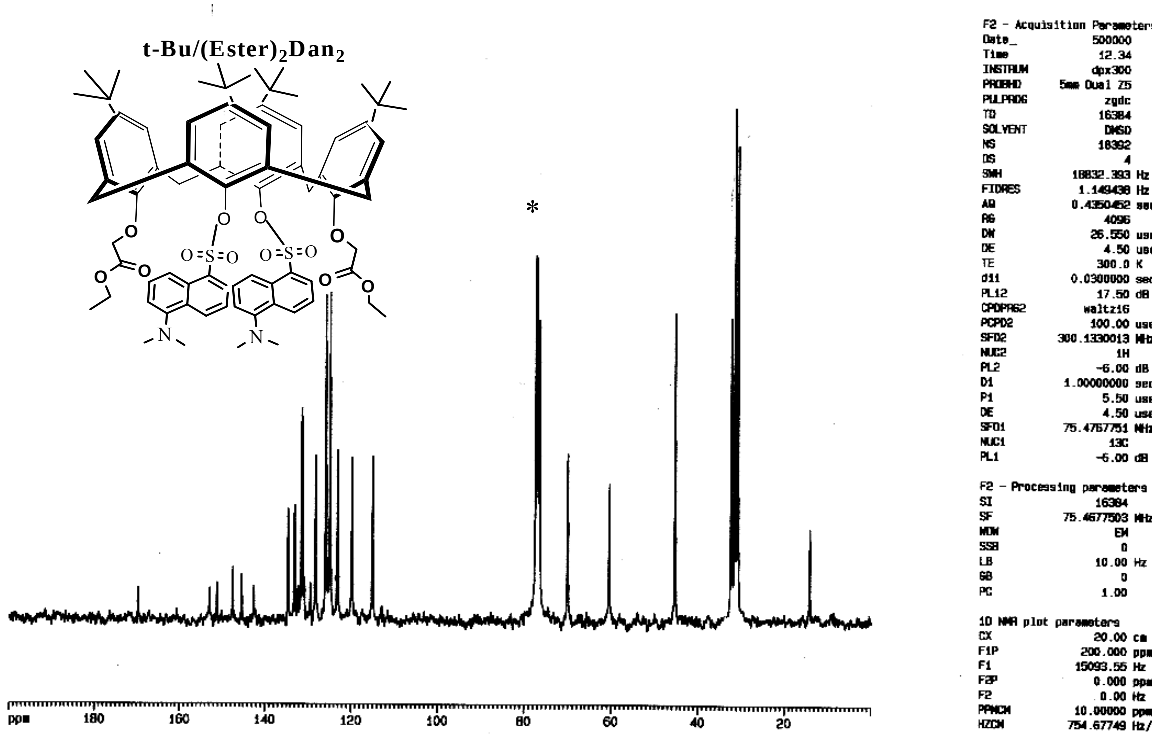
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O=S=O
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N
*
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RG 4096
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TE 300.0 K
d11 0.03000000 sec
PL12 17.50 dB
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 300.1330013 MHz
NUC2 1H
PL2 -6.00 dB
D1 1.00000000 sec
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LB 10.00 Hz
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1D NMR plot parameters
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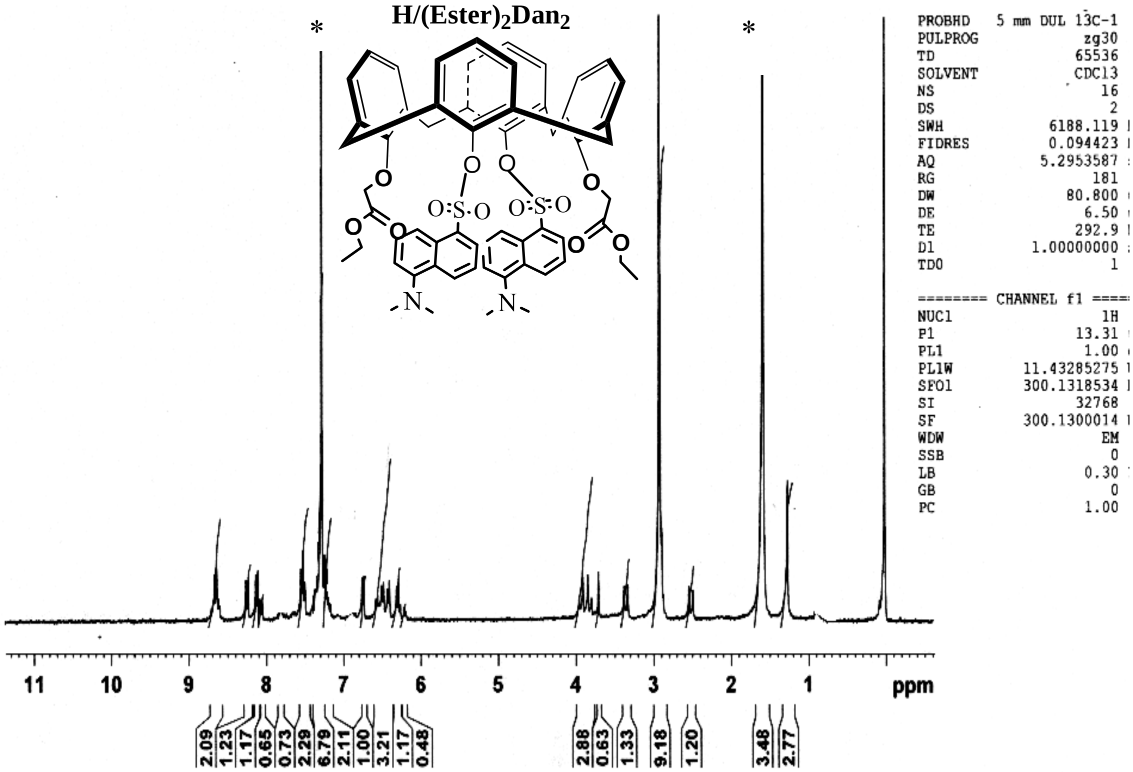

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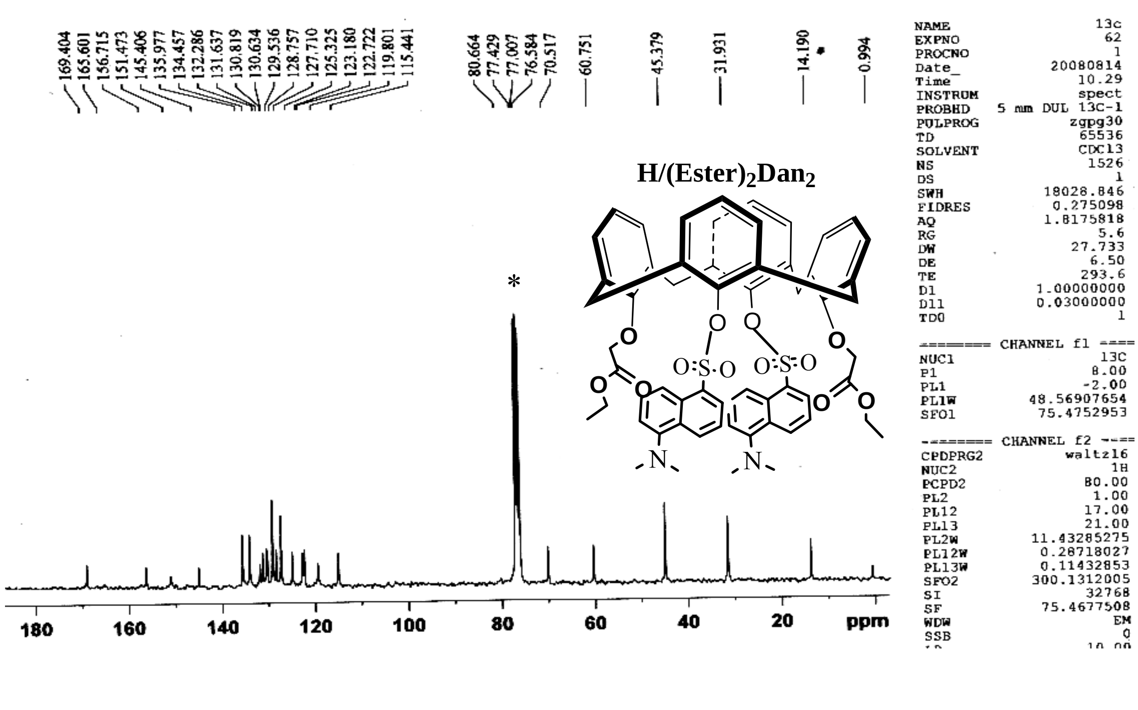
2.88 0.63 1.33 9.18 1.20
3.48 2.77



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45.379
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0.994
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EXPNO 62
PROCNO 1
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INSTRUM spect
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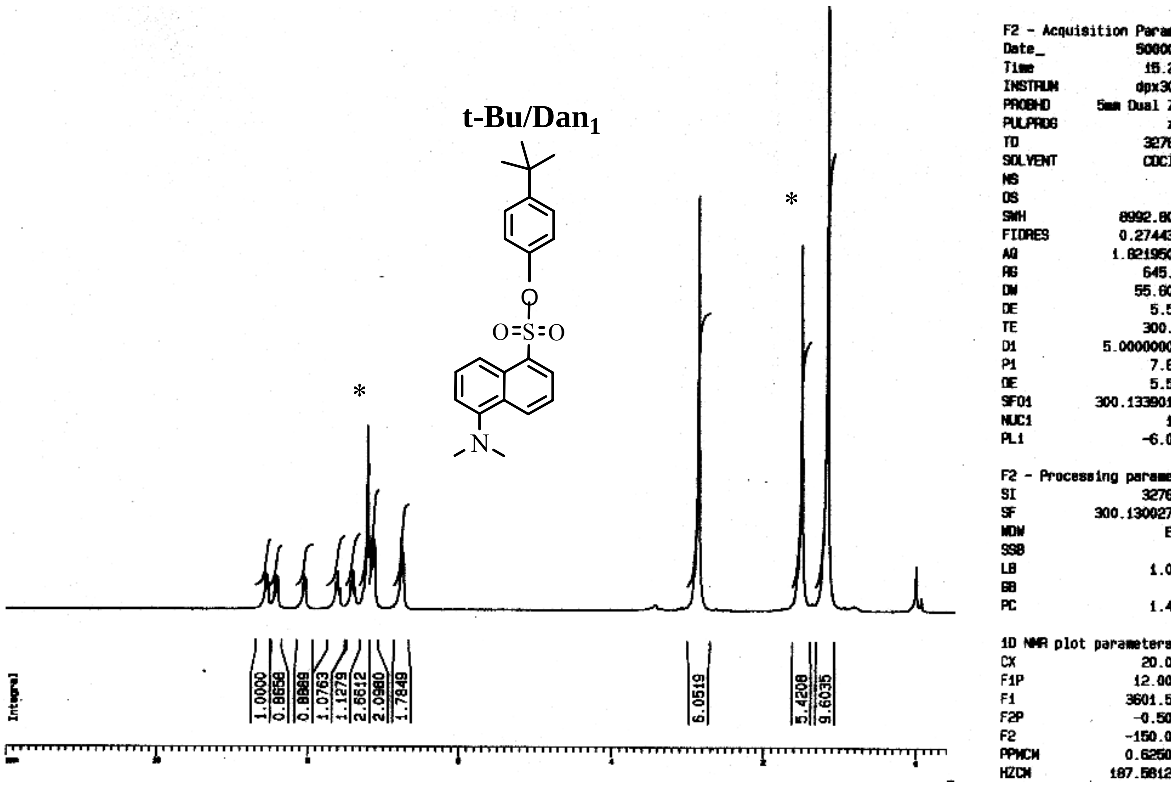
t-Bu/Dan1
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N
*
*
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SOLVENT CDCl
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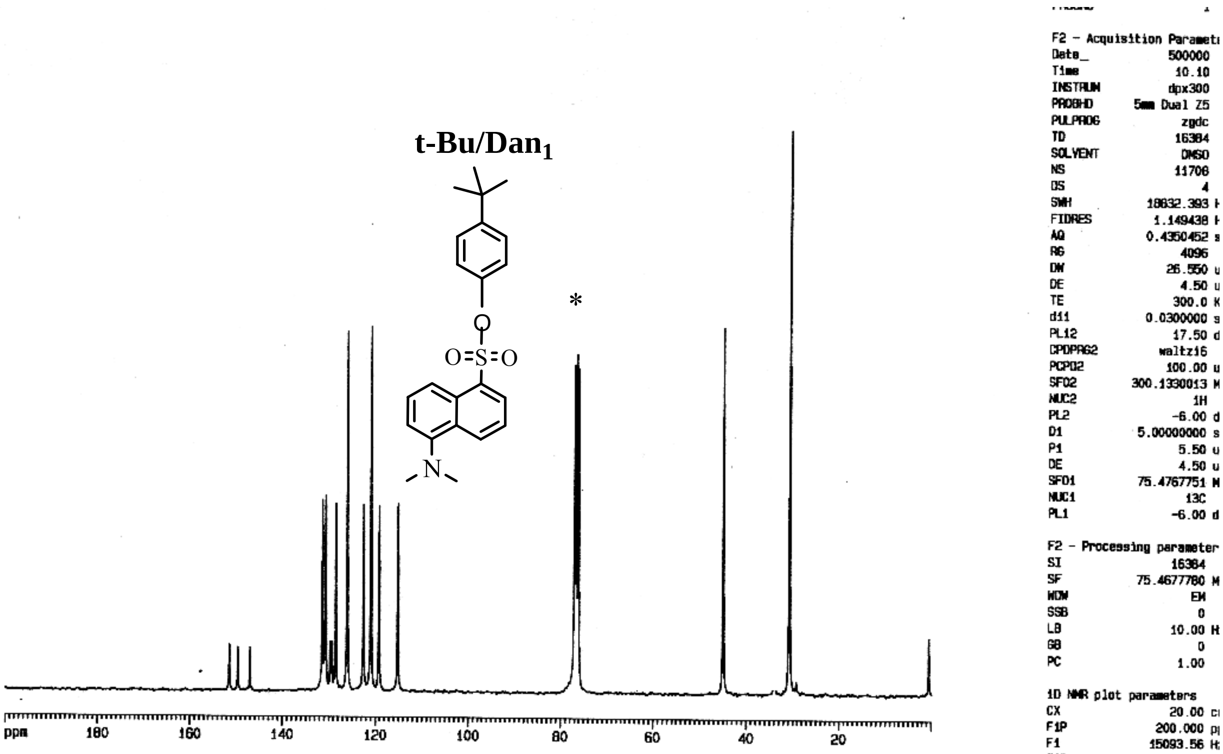
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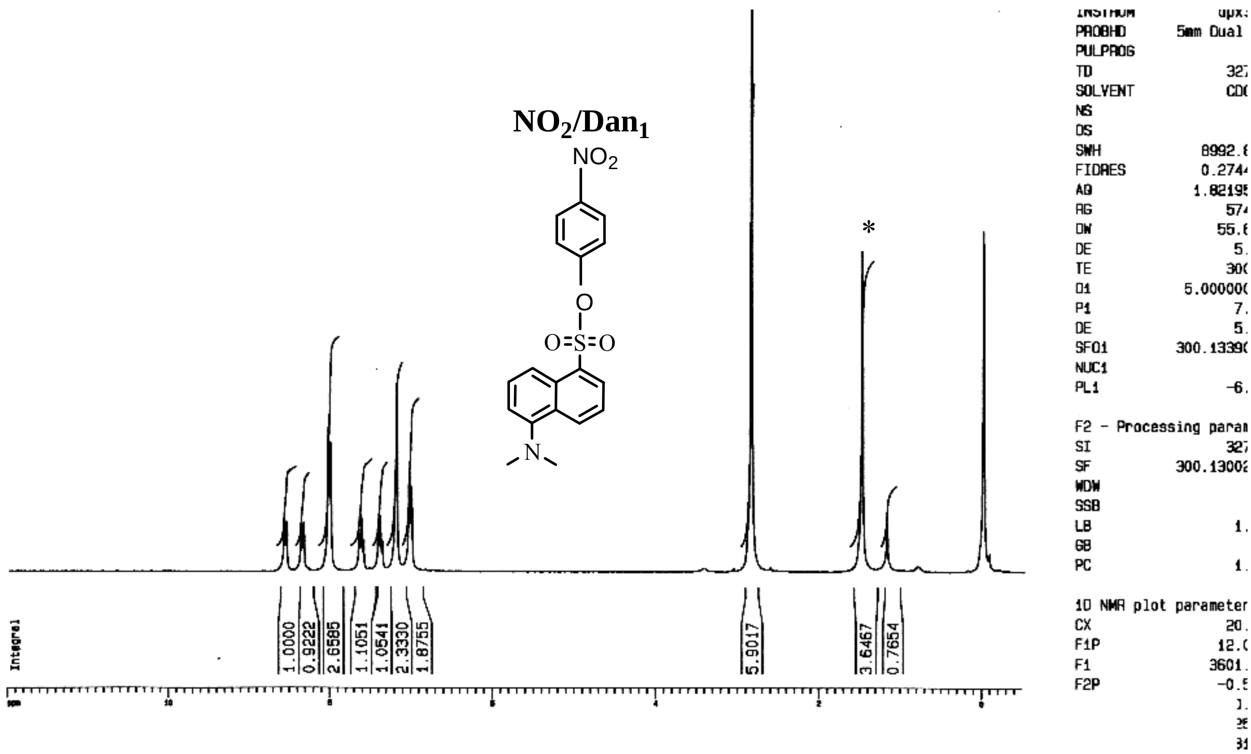
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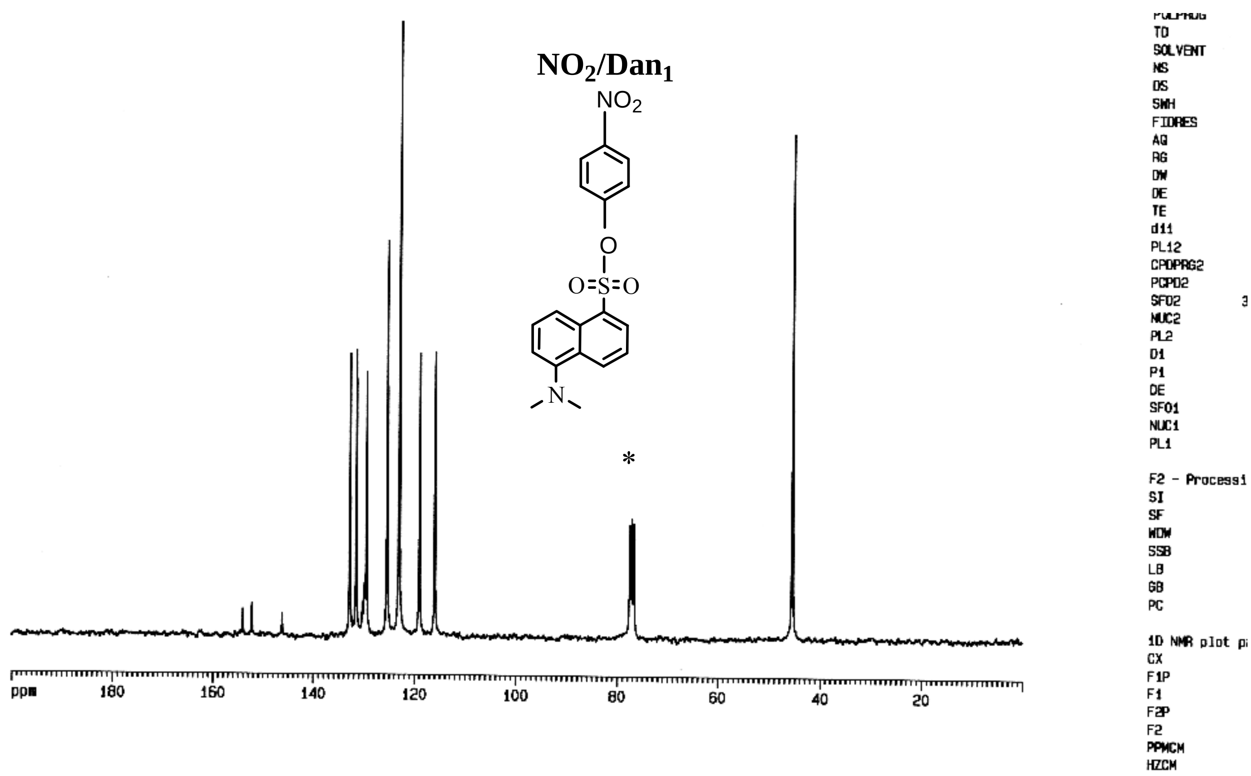
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