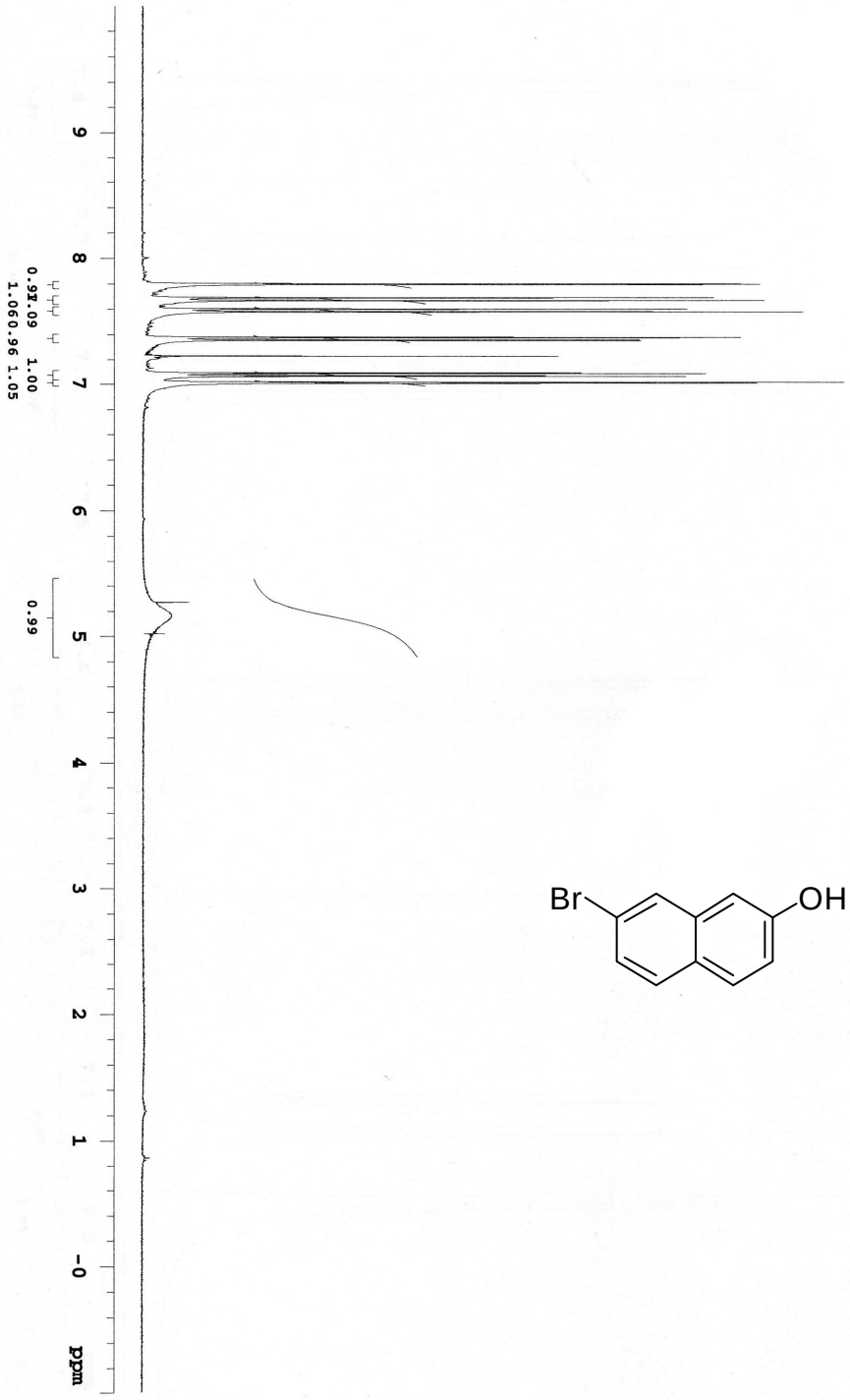
Light-Controlled Supramolecular Helicity of a Liquid Crystalline Phase Using a Helical Polymer Functionalized with a Single Chiroptical Molecular Switch.

Dirk Pijper, Mahthild G. M. Jongejan, Auke Meetsma and Ben L. Feringa*

Department of Organic and Molecular Inorganic Chemistry, Stratingh Institute, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

Fax: (+31)50-363-4296 E-mail: b.l.feringa@rug.nl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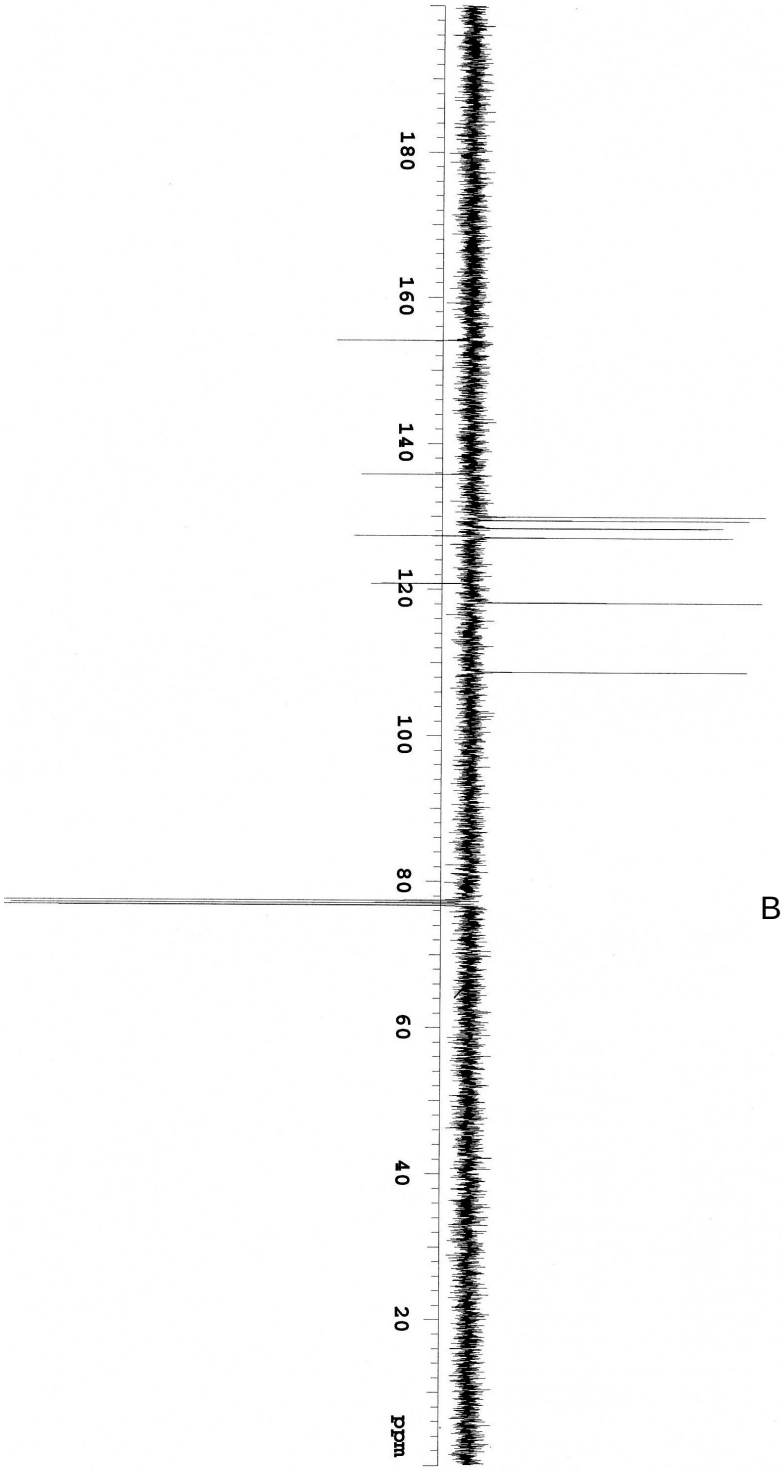
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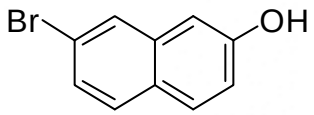
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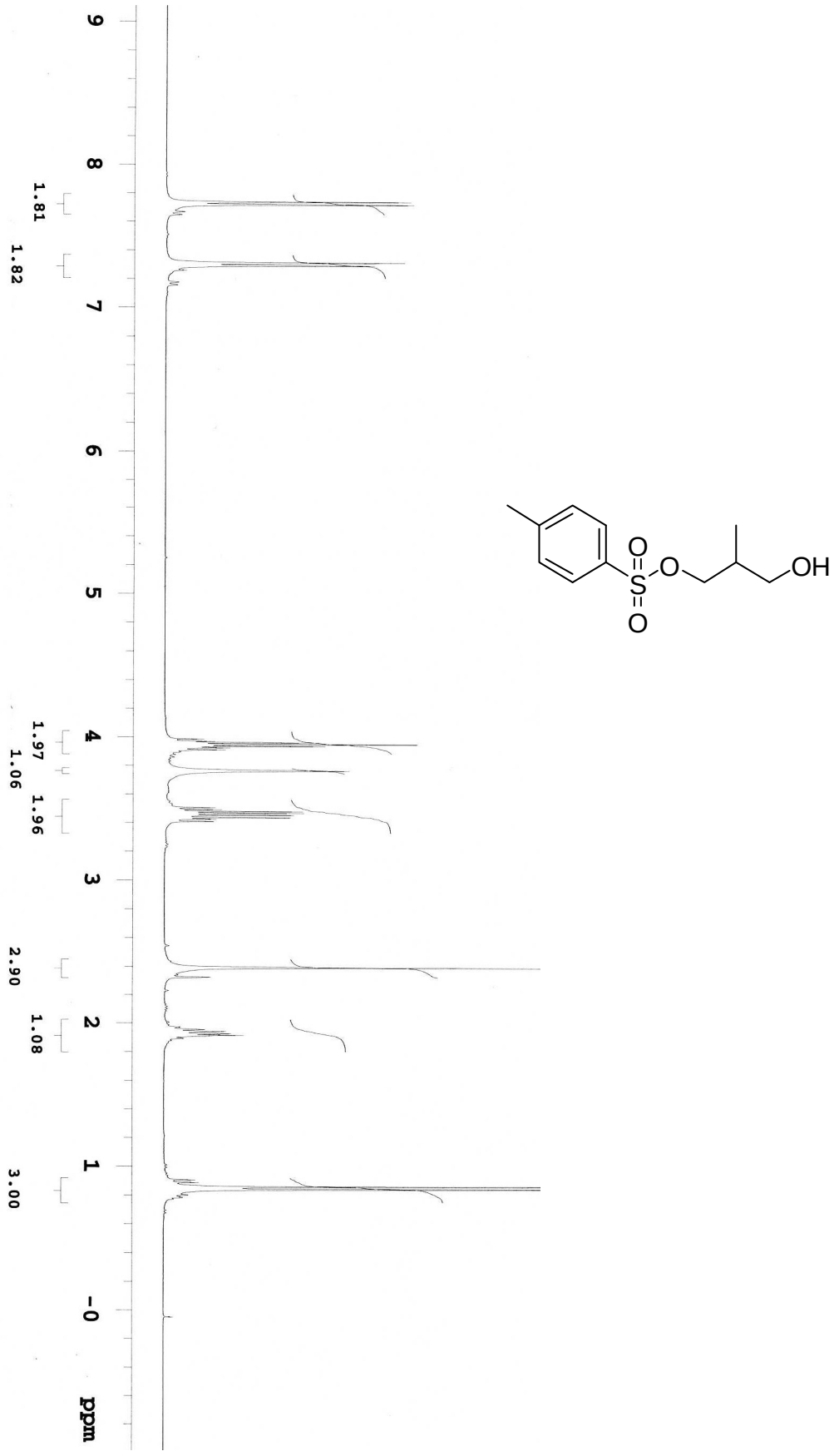
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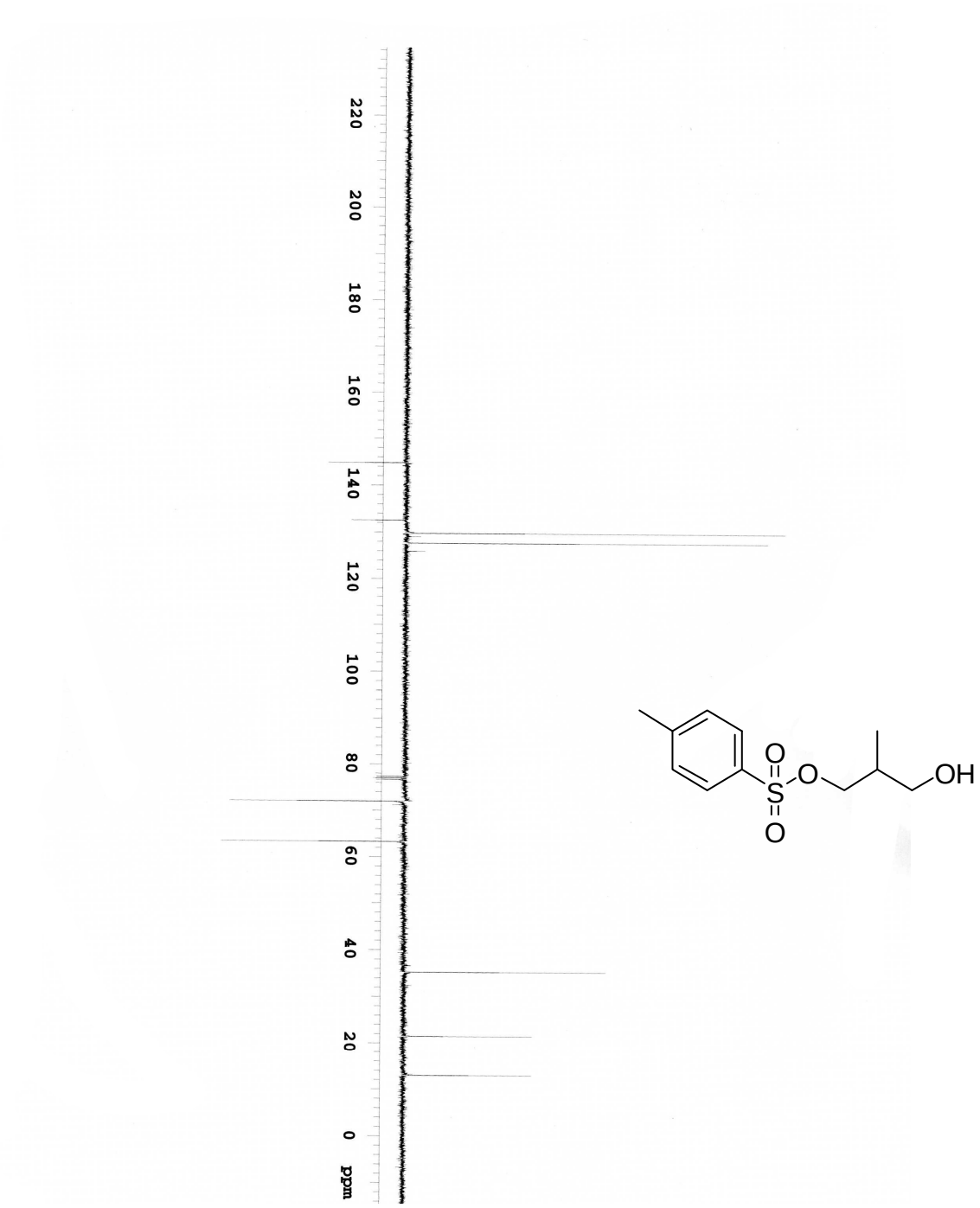
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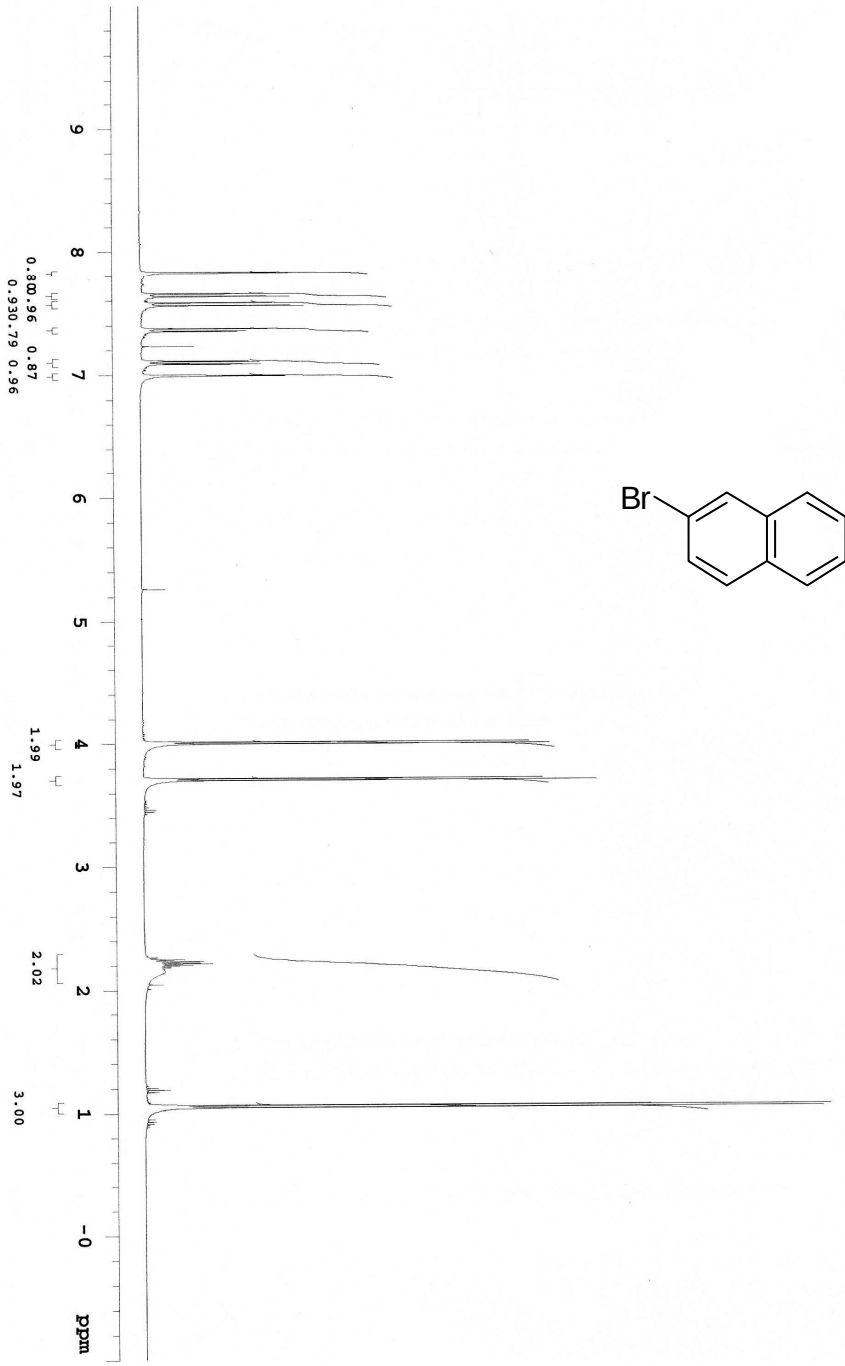
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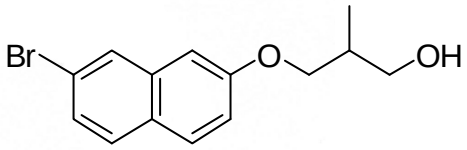
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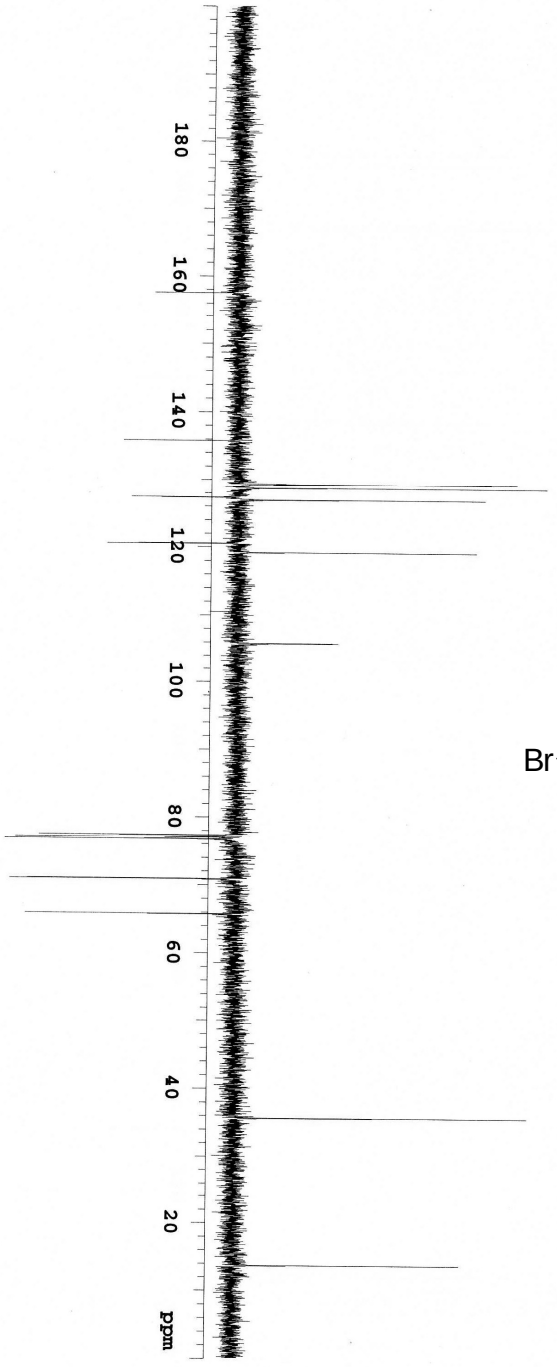
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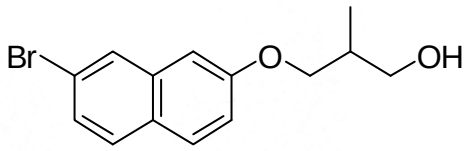
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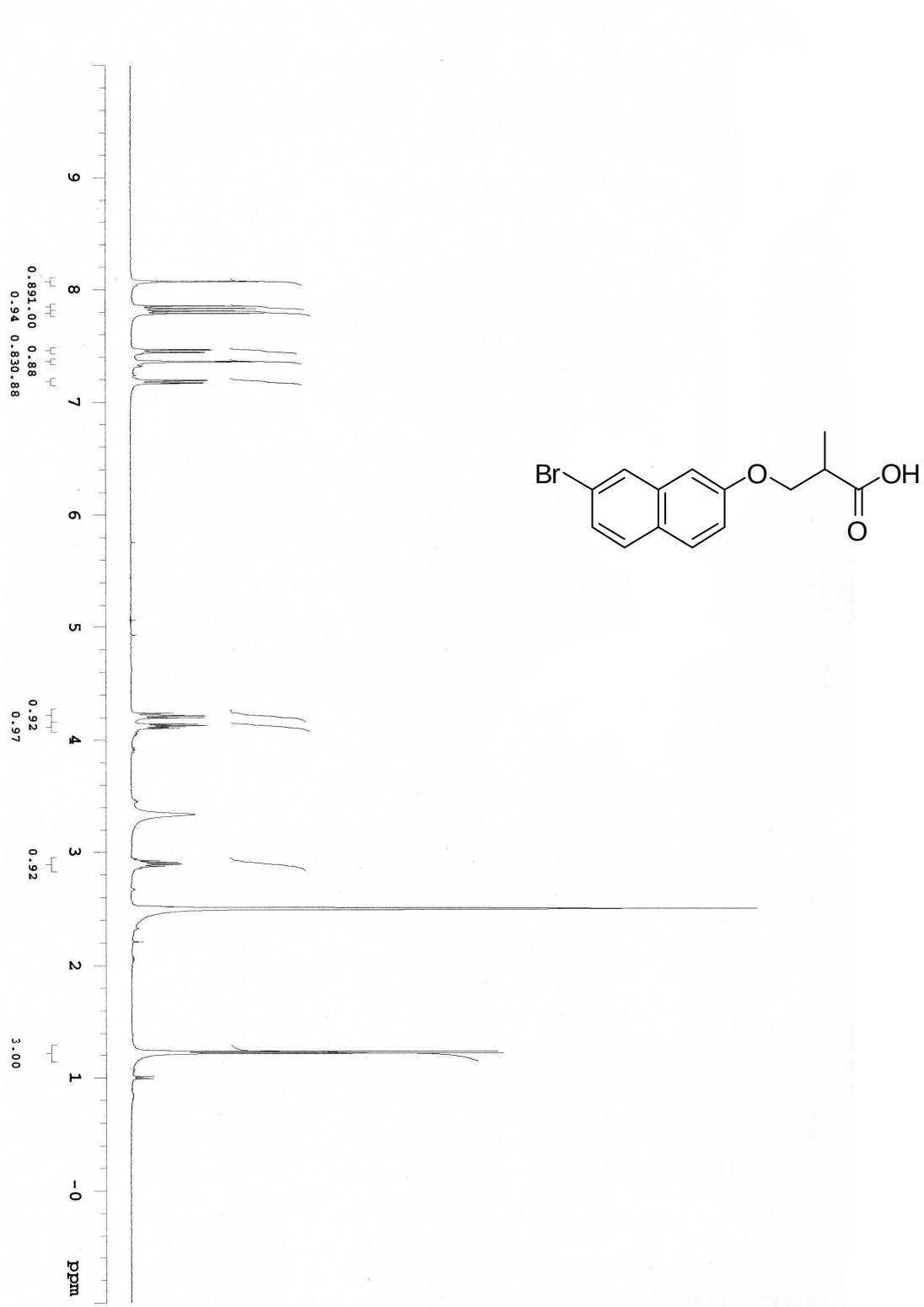
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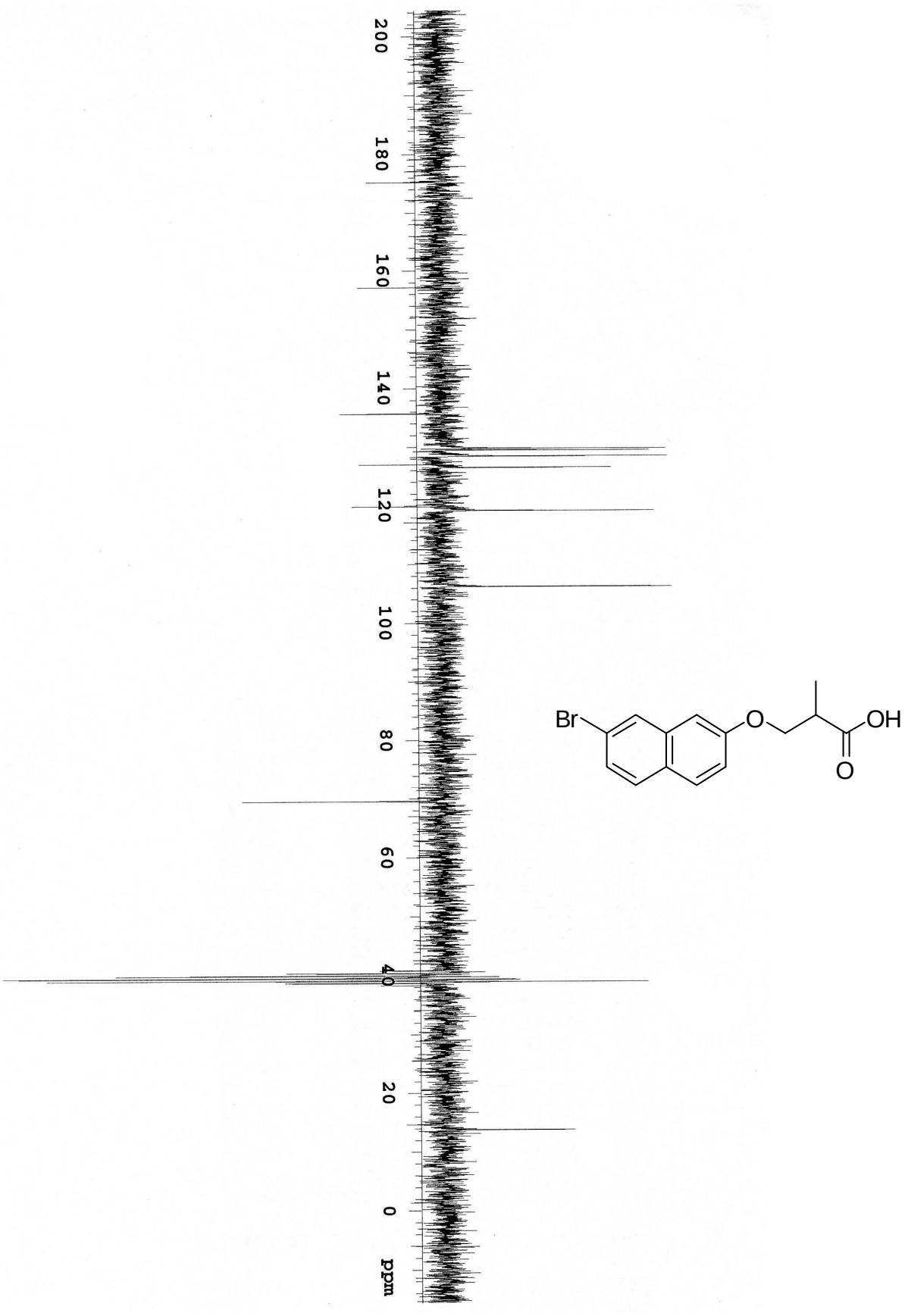
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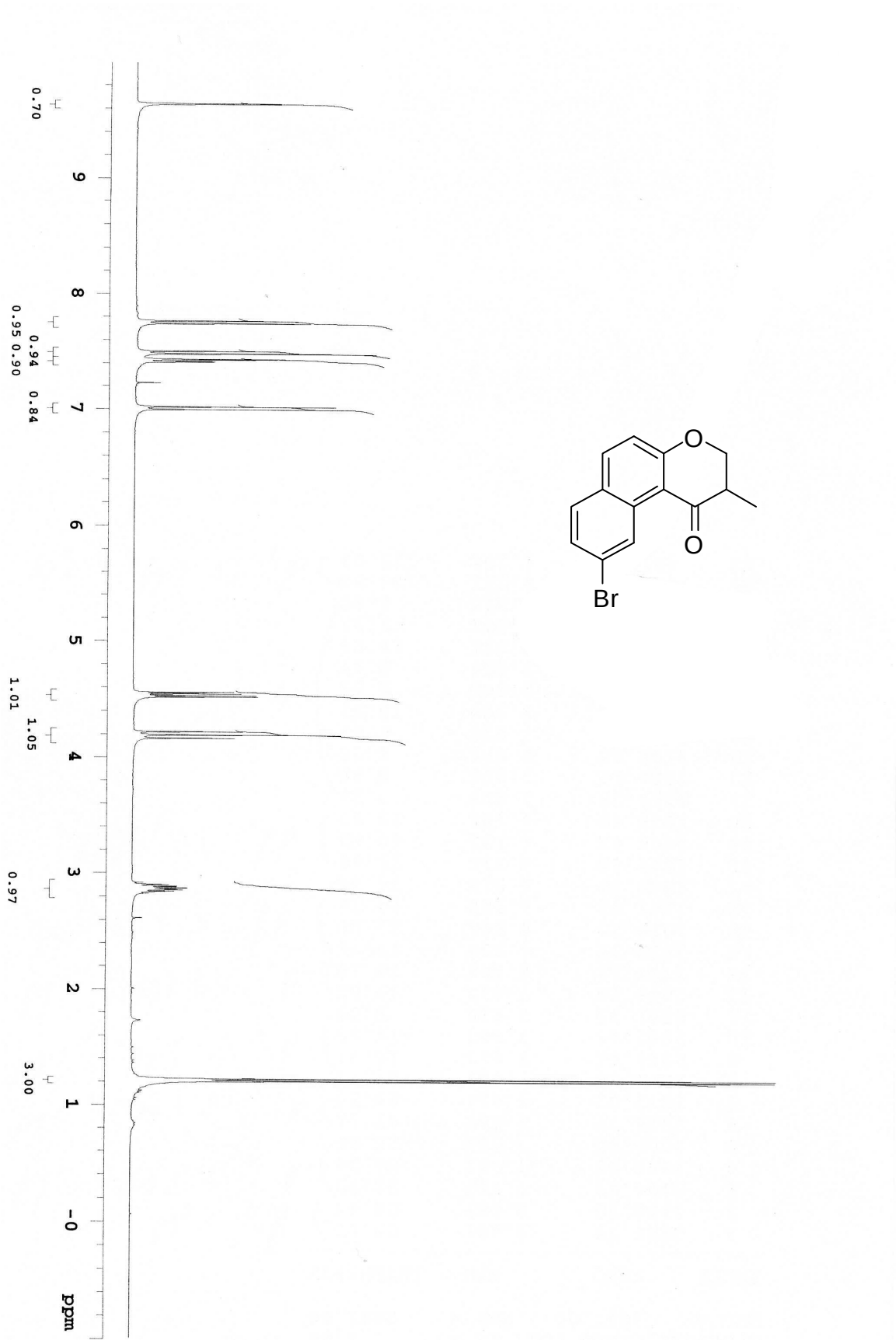
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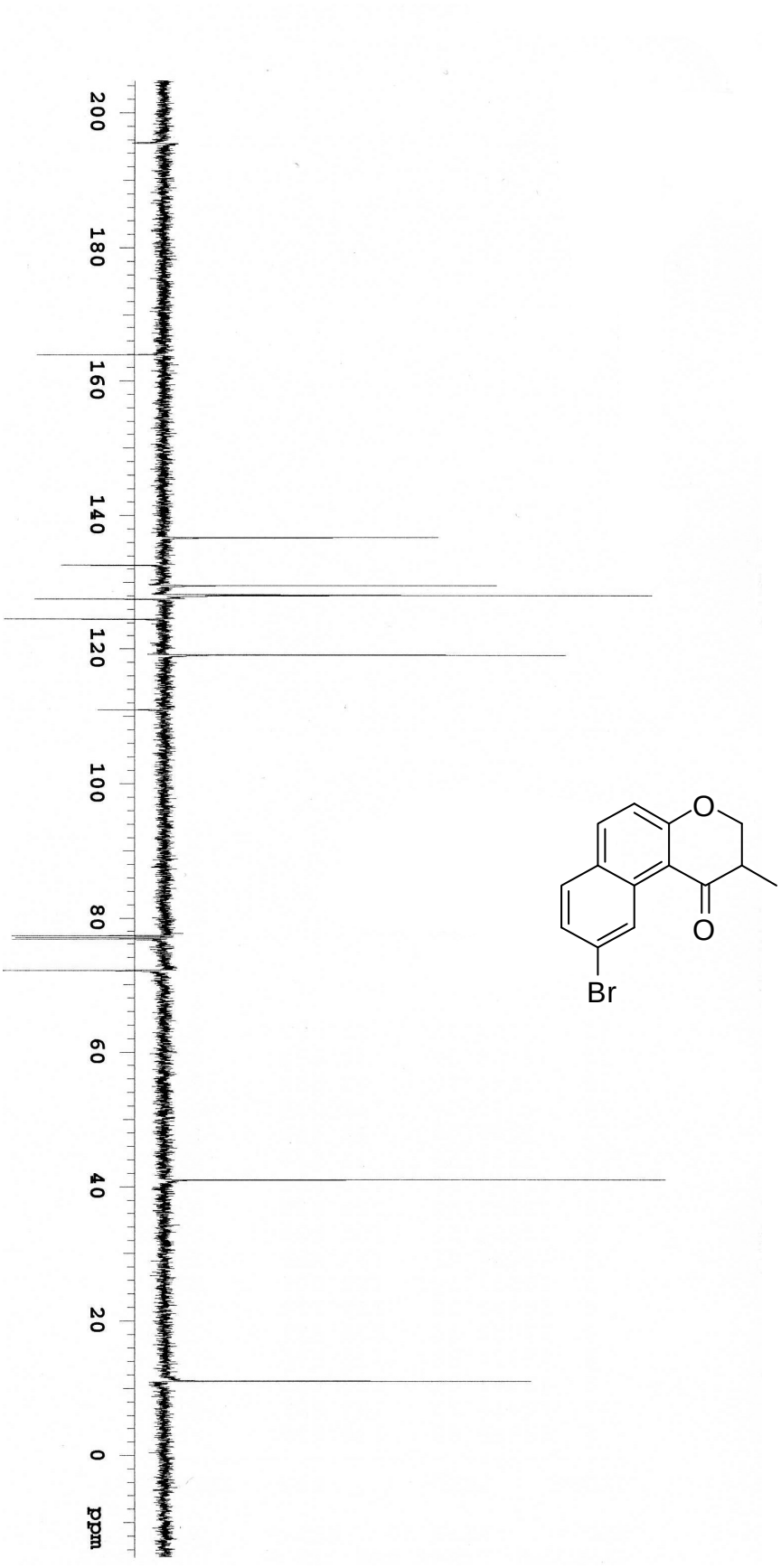
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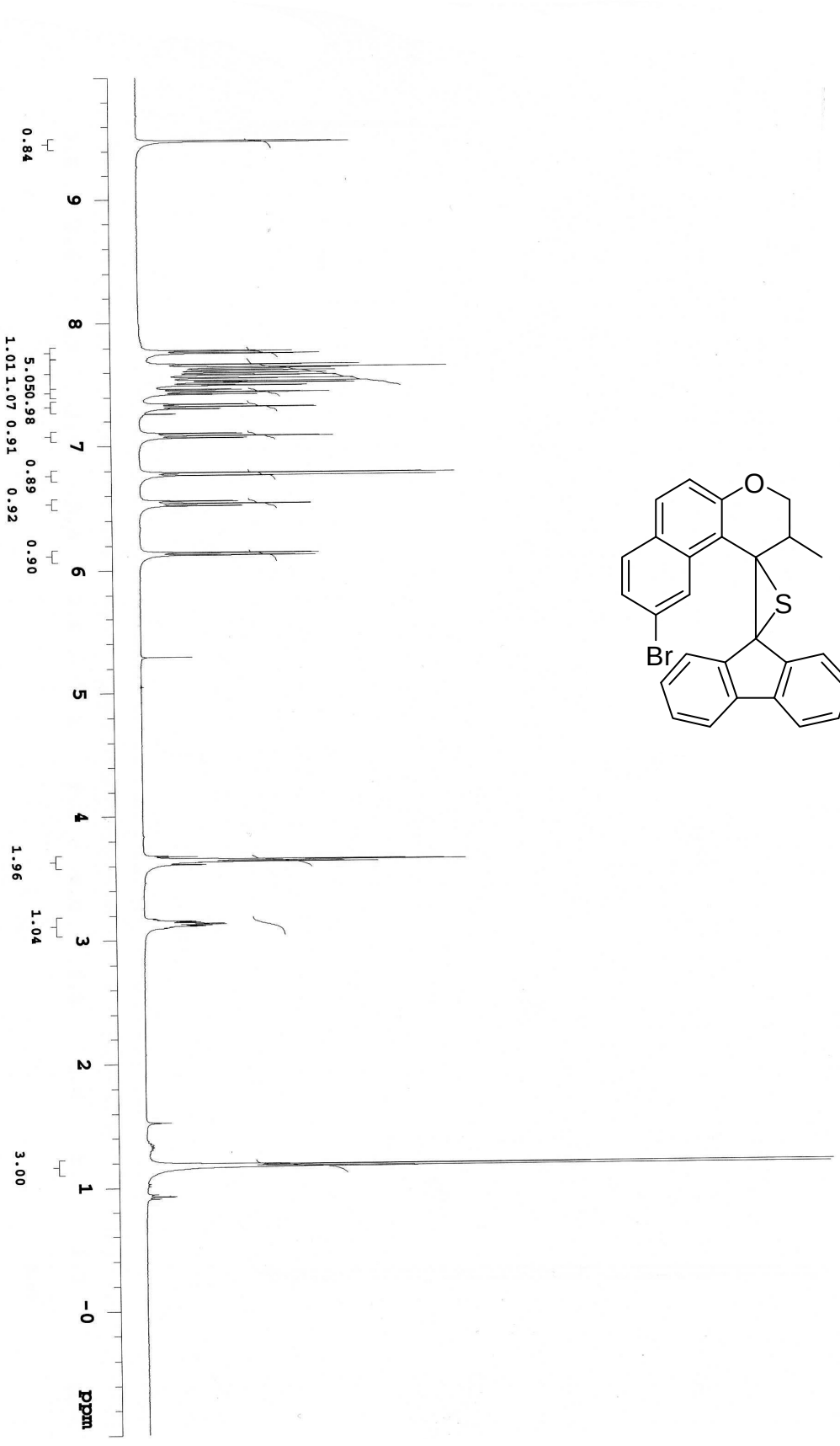
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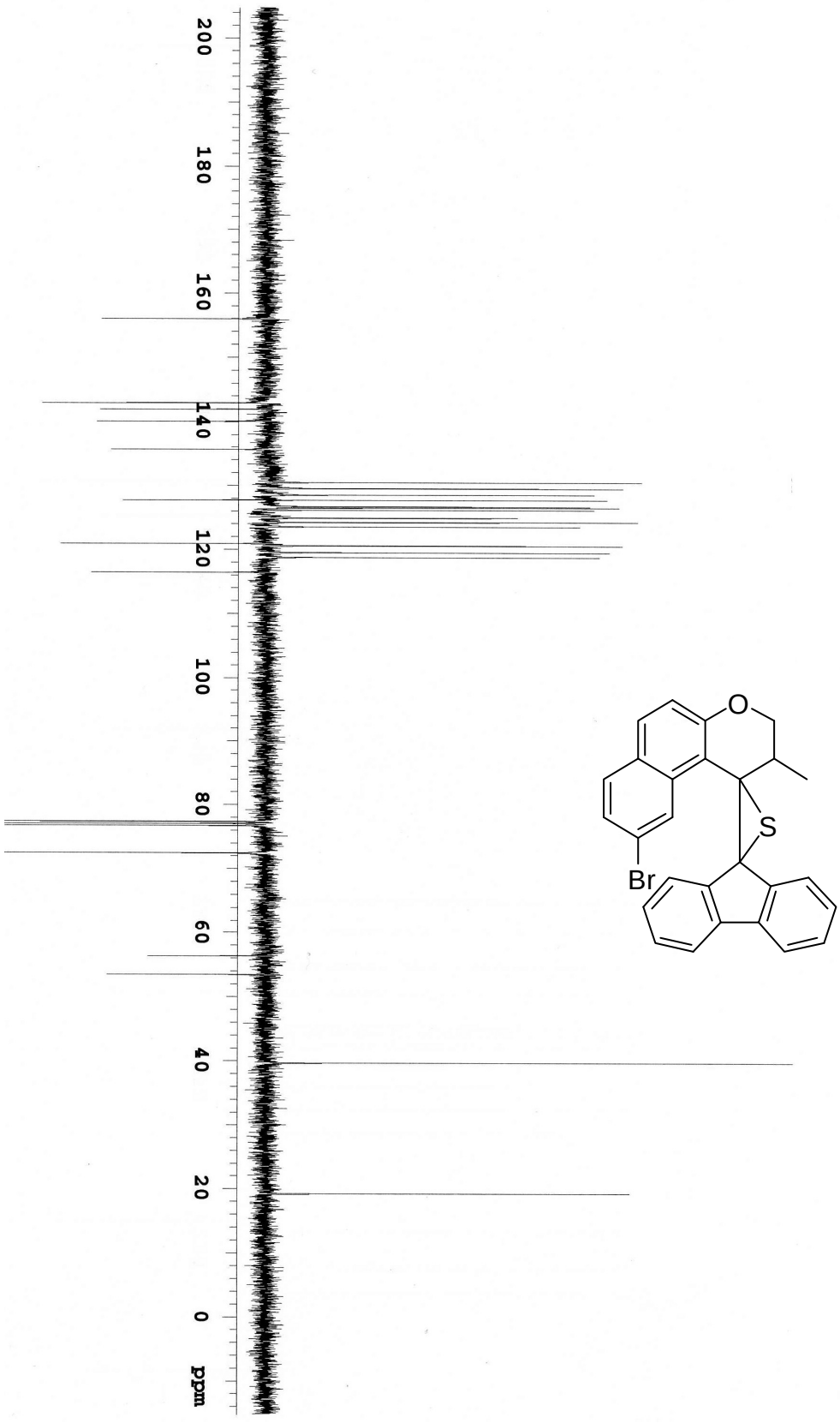
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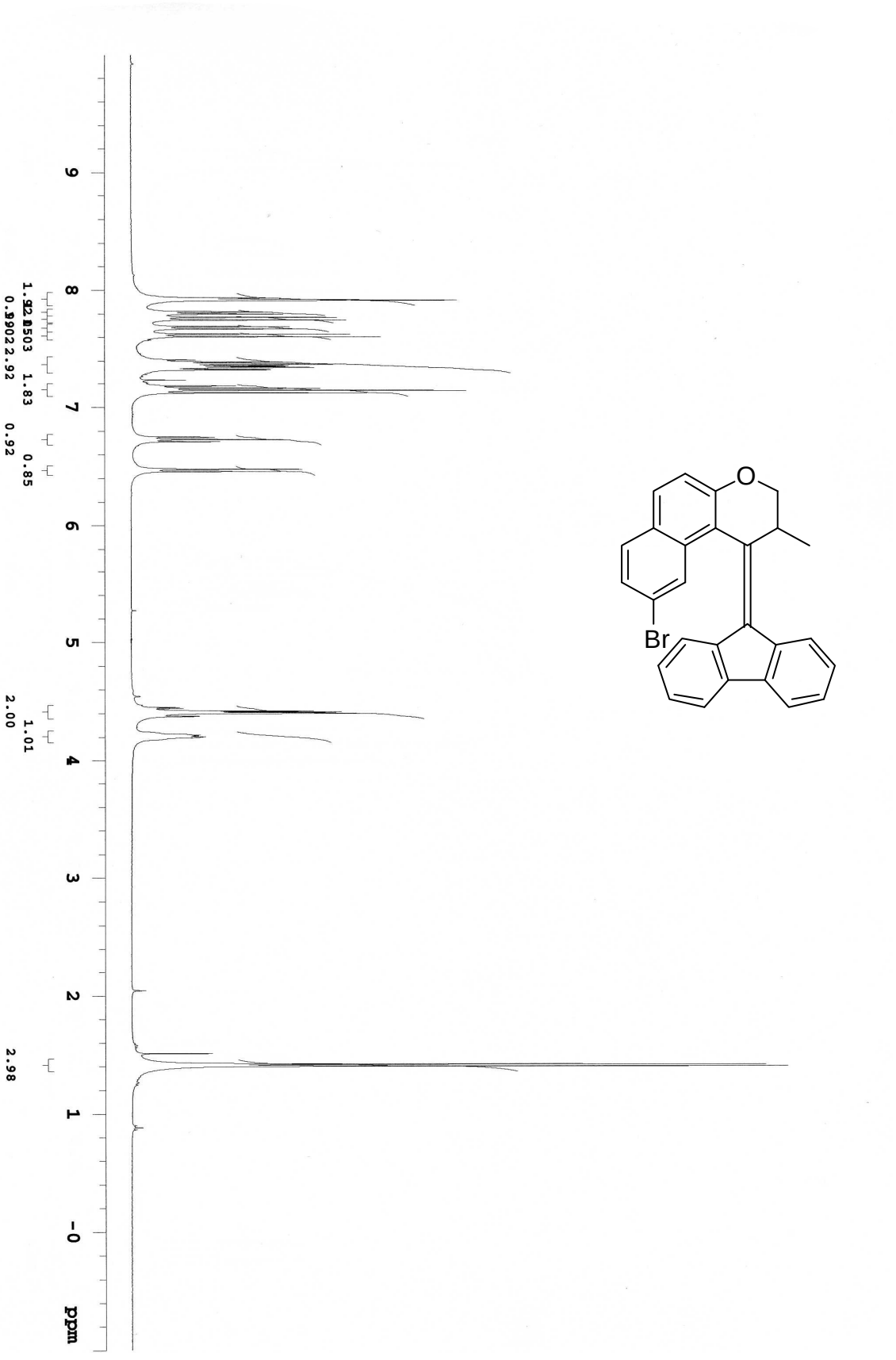
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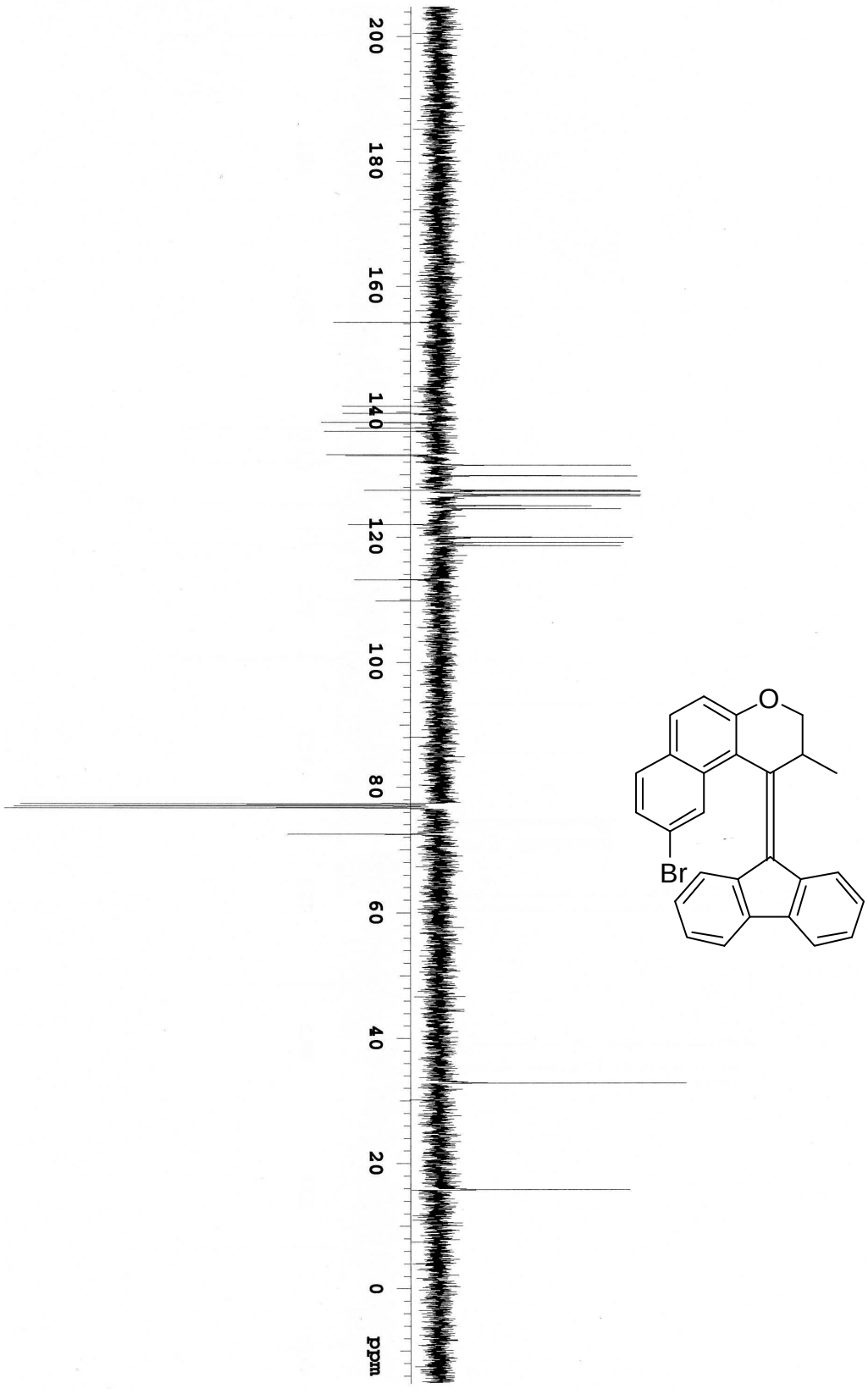
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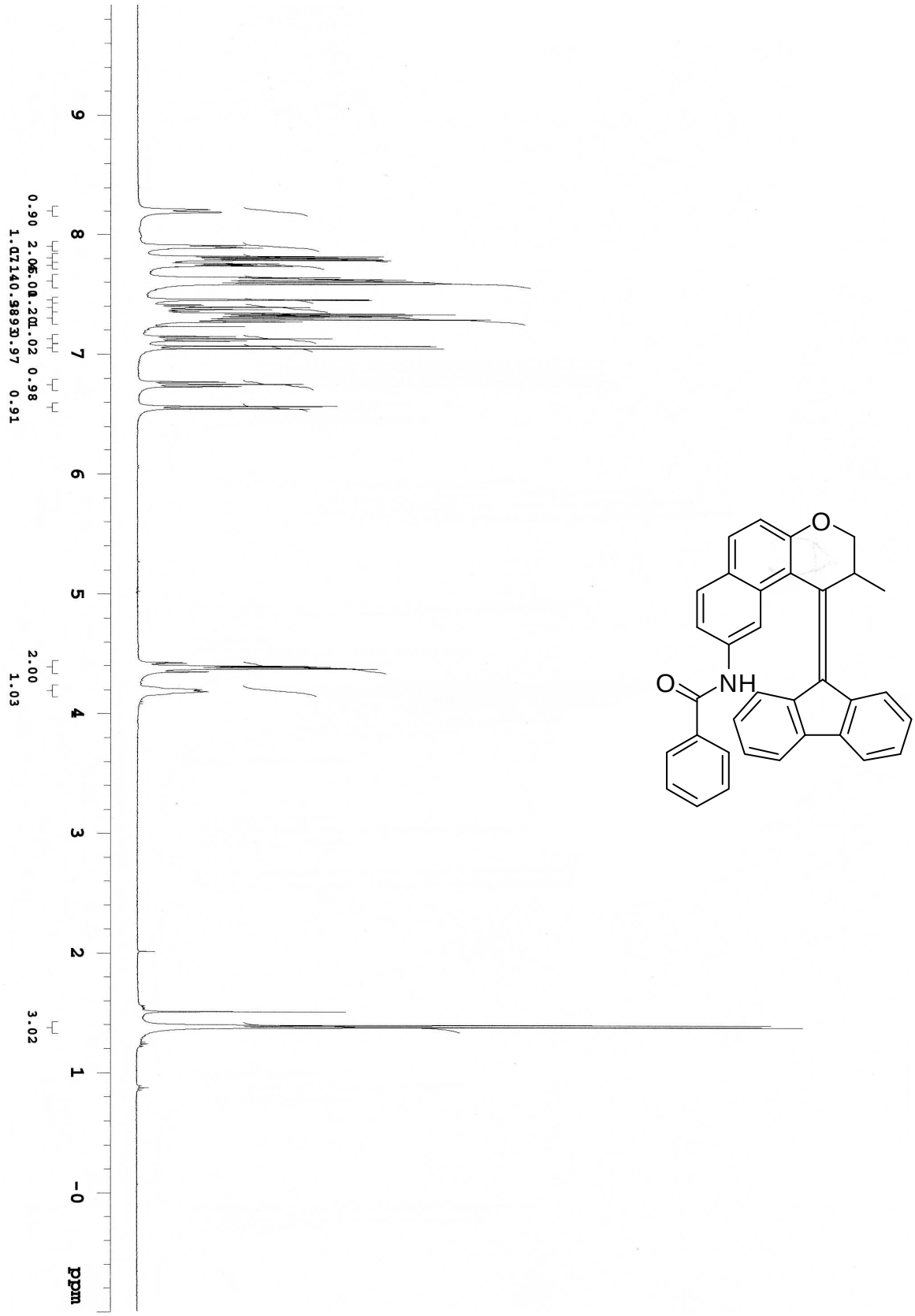
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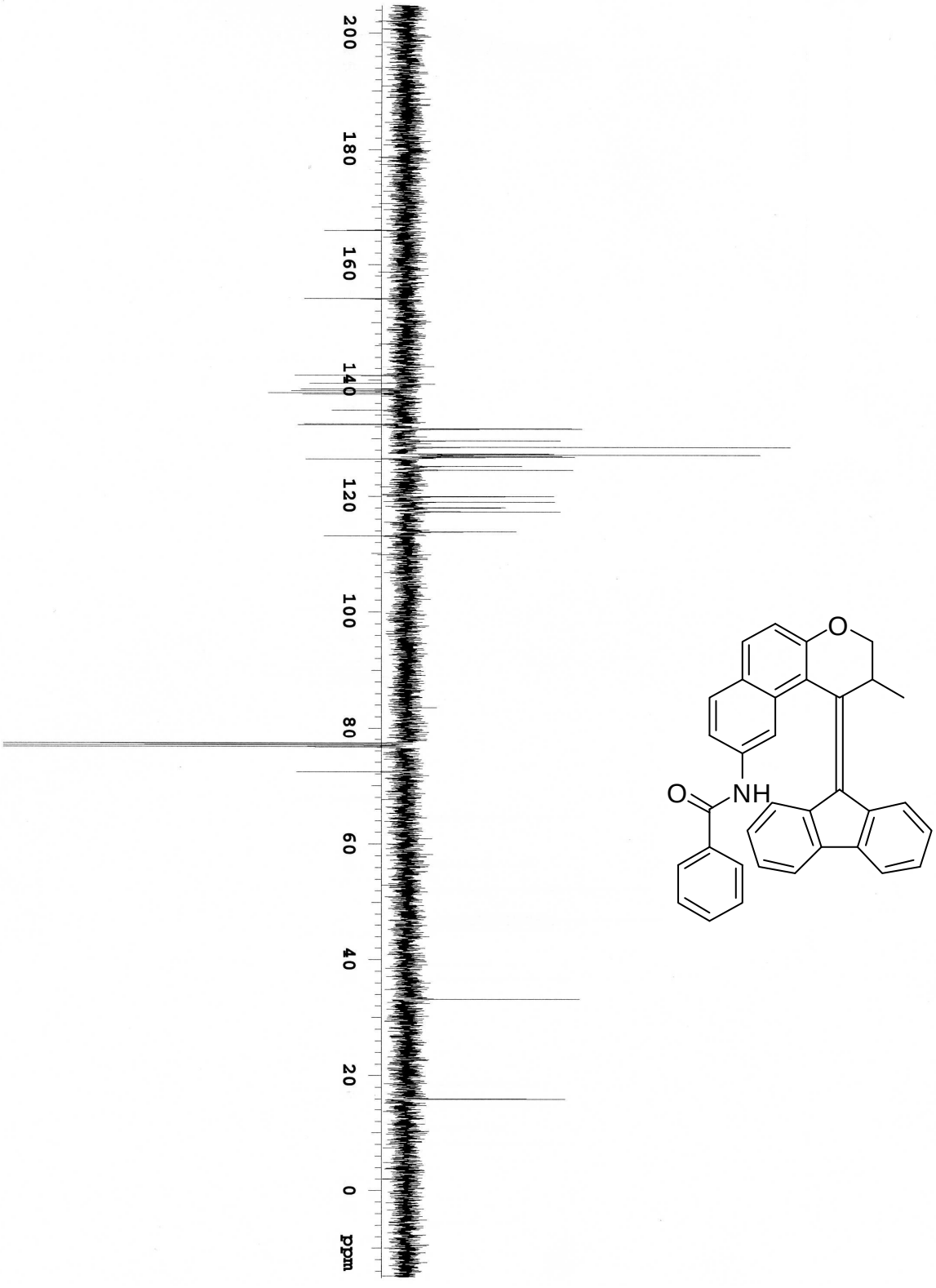
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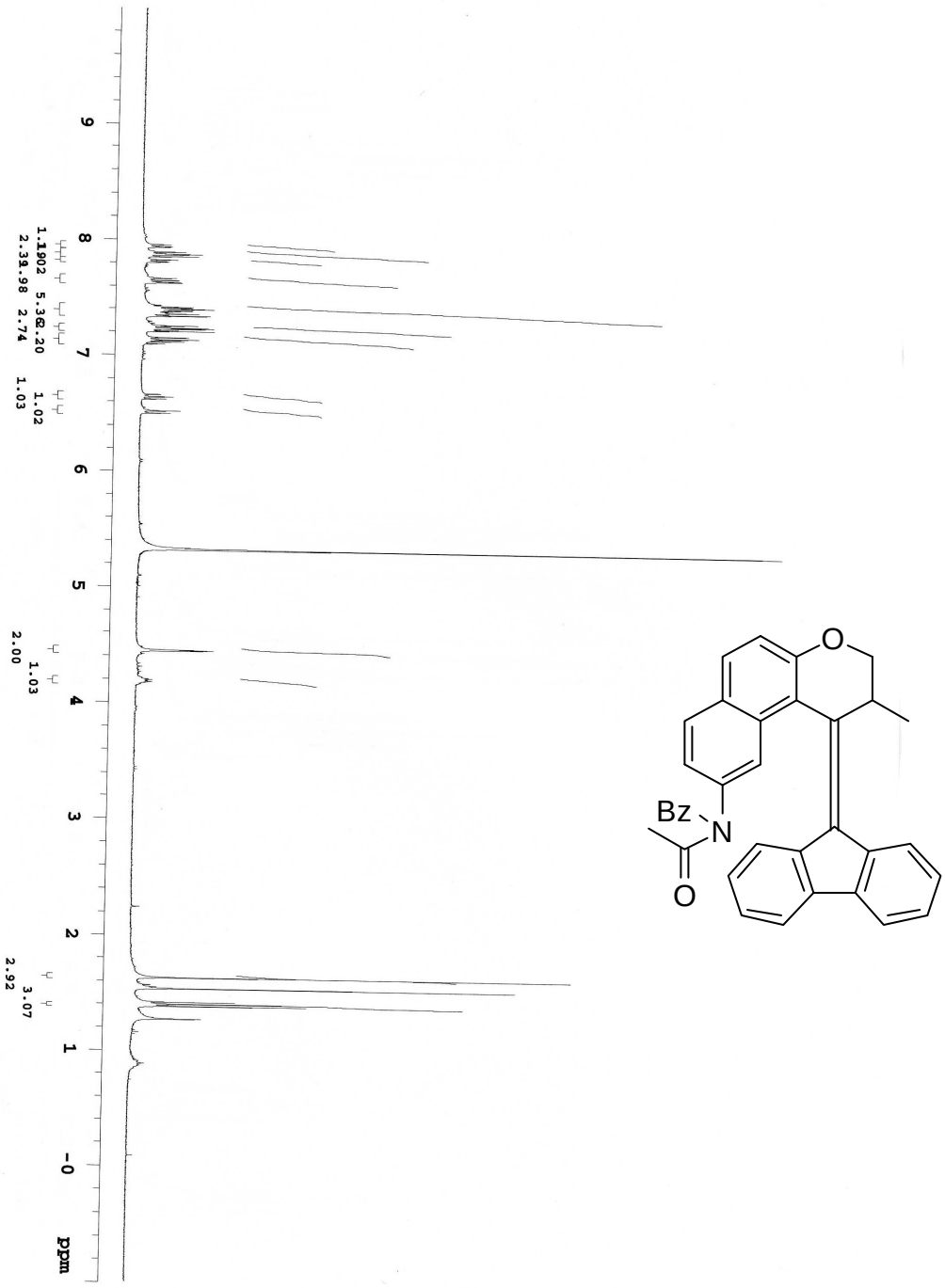
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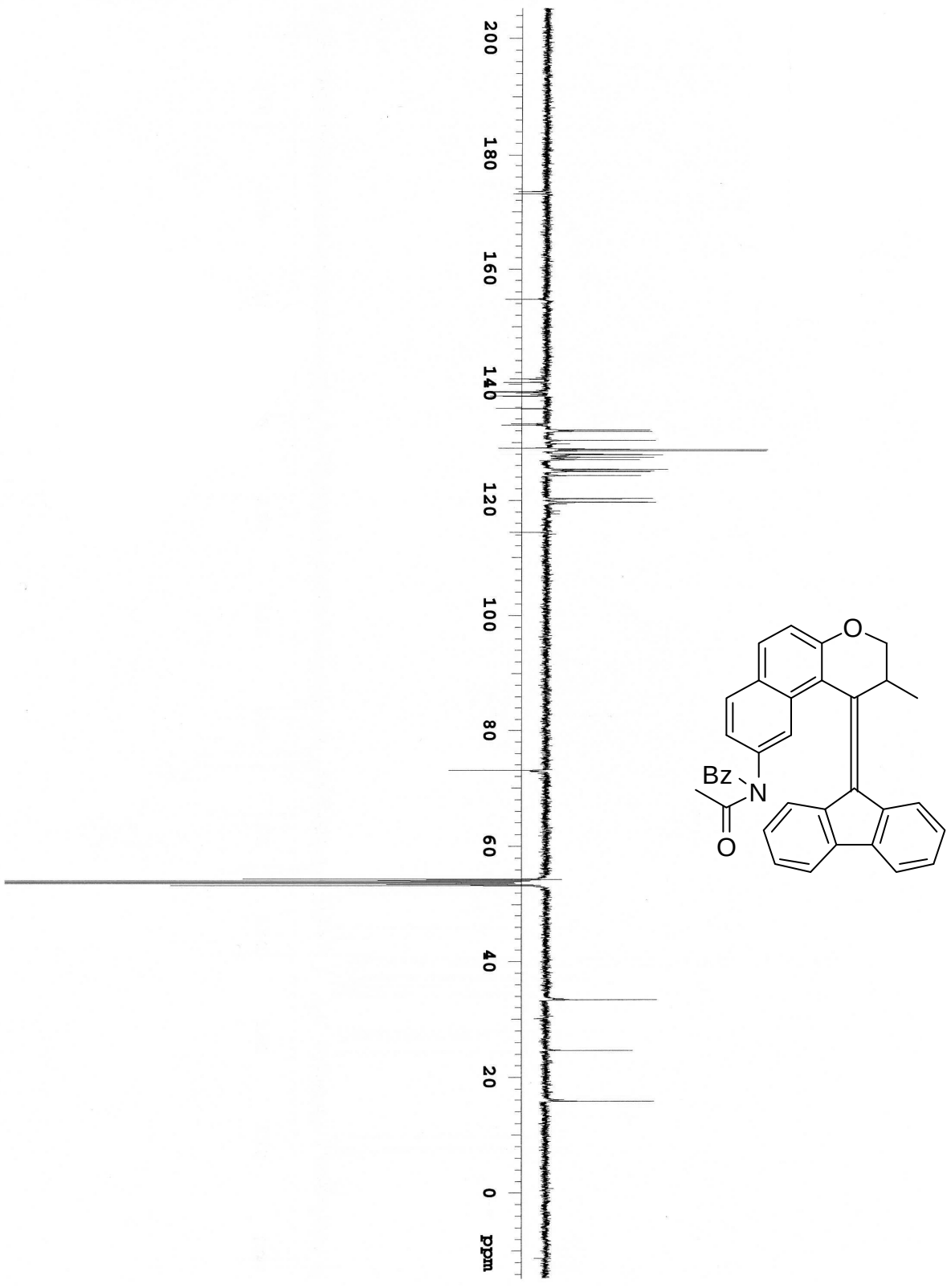
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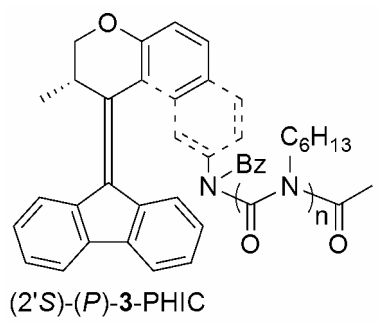
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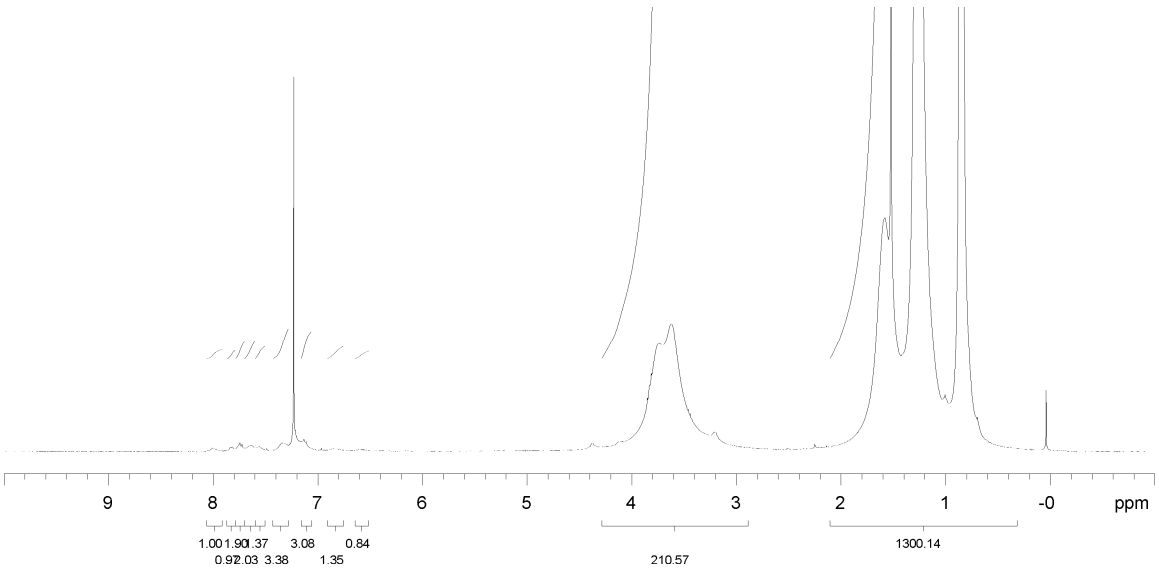
(2'*S*)-(*P*)-**3**-PHIC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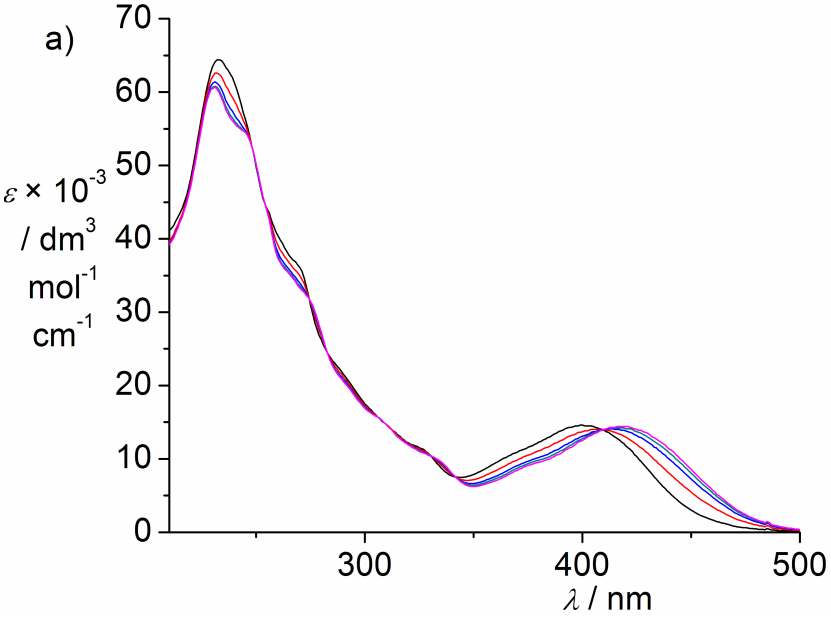
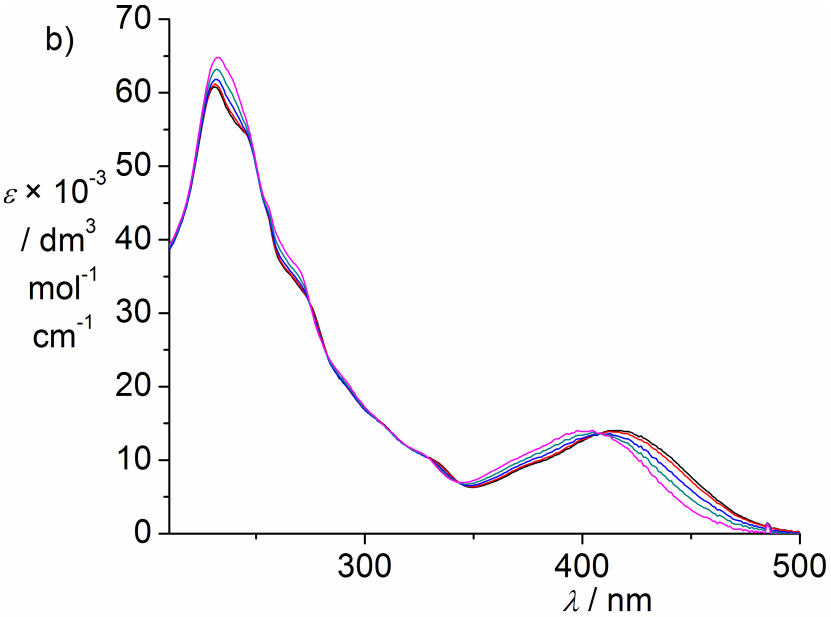


UV/vis spectra (Et_2O, 20°C) of (2*'S*)-(*P*)-**2** (black line), the mixture with (2*'S*)-(*P*)-**2** and (2*'S*)-(*M*)-**2** after 1 min (red), 2 min (blue), 3 min (green), and the PSS mixture after 10 min (magenta) of UV irradiation (λ = 365 nm); clear isosbestic points are observed at 274, 342 and 409 nm.



UV/vis spectra (Et_2O, 20°C) of the PSS mixture with (2*'S*-(*P*)-**2** and (2*'S*-(*M*)-**2** after 10 min of UV irradiation (λ = 365 nm) (black line), the mixture after 45 min (red), 90 min (blue), 150 min (green), and the PSS mixture after 300 min (magenta) of visible light irradiation (λ >480 nm); clear isosbestic points are observed at 274, 342 and 409 nm.

Crystal data and details of the structure determination of (2'*S)-(*P**)-2 and (2'*S**)-(*M**)-2.**

Moiety_Formula	$C_{34}H_{25}NO_2$
Formula_Weight, g.mol^{-1}	479.58
Crystal system	orthorhombic
Space group, no.	$P2_12_12_1$, 19
a, Å	9.1089 (13)
b, Å	13.2614 (18)
c, Å	19.958 (3)
V, Å	2410.9 (6)
Θ range unit cell: min.-max., deg; reflections	2.55 - 27.31 ; 6046
Formula_*Z*	4
SpaceGroup_*Z*	4
Z' (= Formula_*Z* / SpaceGroup_*Z*)	1
ρ_{calc}, g.cm^{-3}	1.321
F(000), electrons	1008
μ(Mo K$\bar{\alpha}$), cm^{-1}	0.81
Color, habit	orange, block
Approx. crystal dimension, mm	0.37 x 0.14 x 0.12

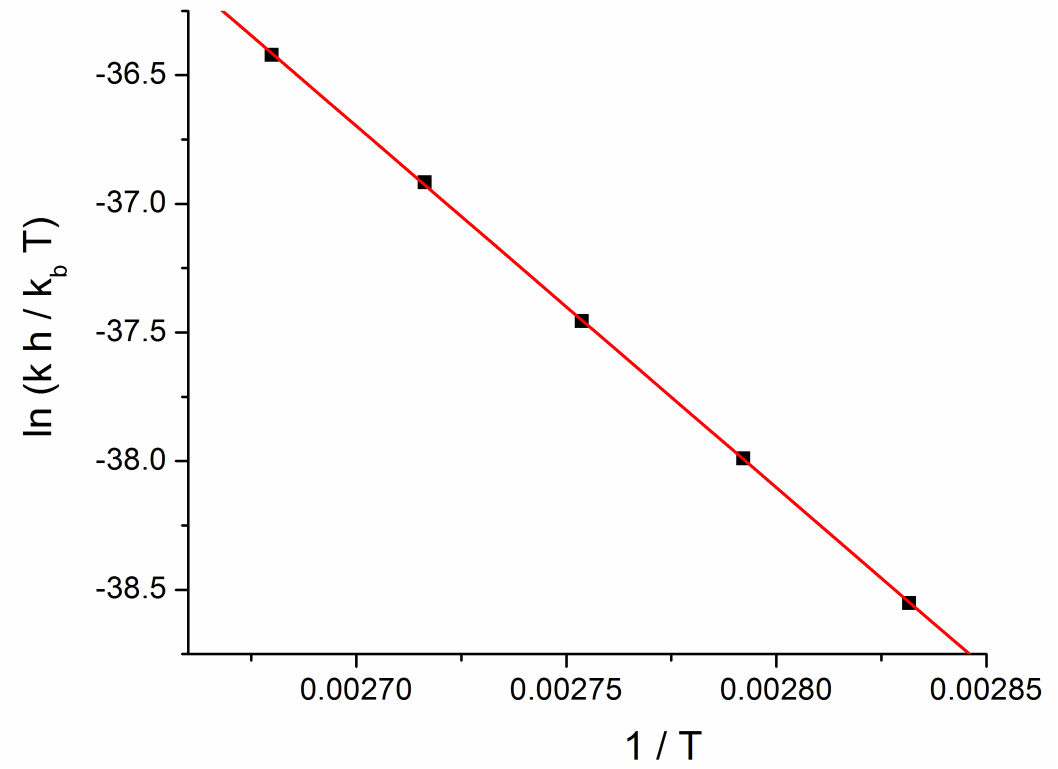
a. Data collection.

λ(Mo K$\bar{\alpha}$), Å	0.71073
Monochromator	Graphite
Measurement device type	Bruker SMART APEX CCD area-detector diffractometer
Detector Area resolution (pixels / mm)	4096 x 4096 / 62 x 62 (binned 512)
Temperature, K	100 (1)
Measurement method	φ- and ω-scans
θ range; min. max., deg	2.46, 25.34
Index ranges	h: -10→10; k: -15→14; l: -22→23
Min.- Max. absorption transmission factor	0.9603 – 0.9903
X-ray exposure time, h	16.6 (30 sec / frame)
Total data	15811
Unique data	2495
Data with criterion: ($F_o \geq 4.0\ \sigma\ (F_o)$)	2145
$R_{int} = \sum [\lvert F_o^2 - F_o^2(\text{mean})\rvert] / \sum [F_o^2]$	0.0701
$R_{sig} = \sum \sigma(F_o^2) / \sum [F_o^2]$	0.0645

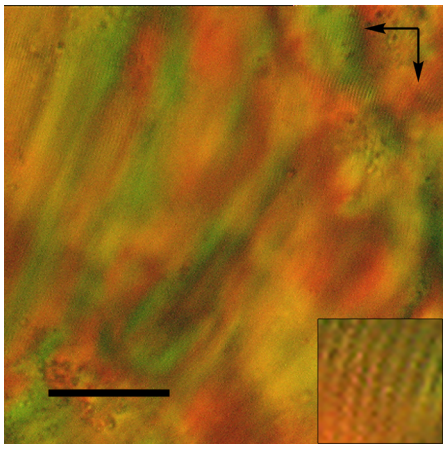
b. Refinement.

Number of reflections	2495
Number of refined parameters	431
Final agreement factors:	
$wR(F^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$	0.0997
Weighting scheme: a, b	0.0, 1.4636
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$	
And $P = [\max(F_o^2,0) + 2F_c^2] / 3$	
$R(F) = \sum (\|\|F_o\| - \|F_c\|\|) / \sum \|F_o\|$	0.0461
For $F_o > 4.0\ \sigma\ (F_o)$	
$GooF = S = [\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$	1.068
n = number of reflections	
p = number of parameters refined	
Residual electron density in final	
Difference Fourier map, e/Å^3	-0.40, 0.36 (4)
Max. (shift/σ) final cycle	<0.001
Average (shift/σ) final cycle	<0.001

Eyring plot for the thermal conversion of (2'*S*)-(*M*)-**2** to (2'*S*)-(*P*)-**2**:

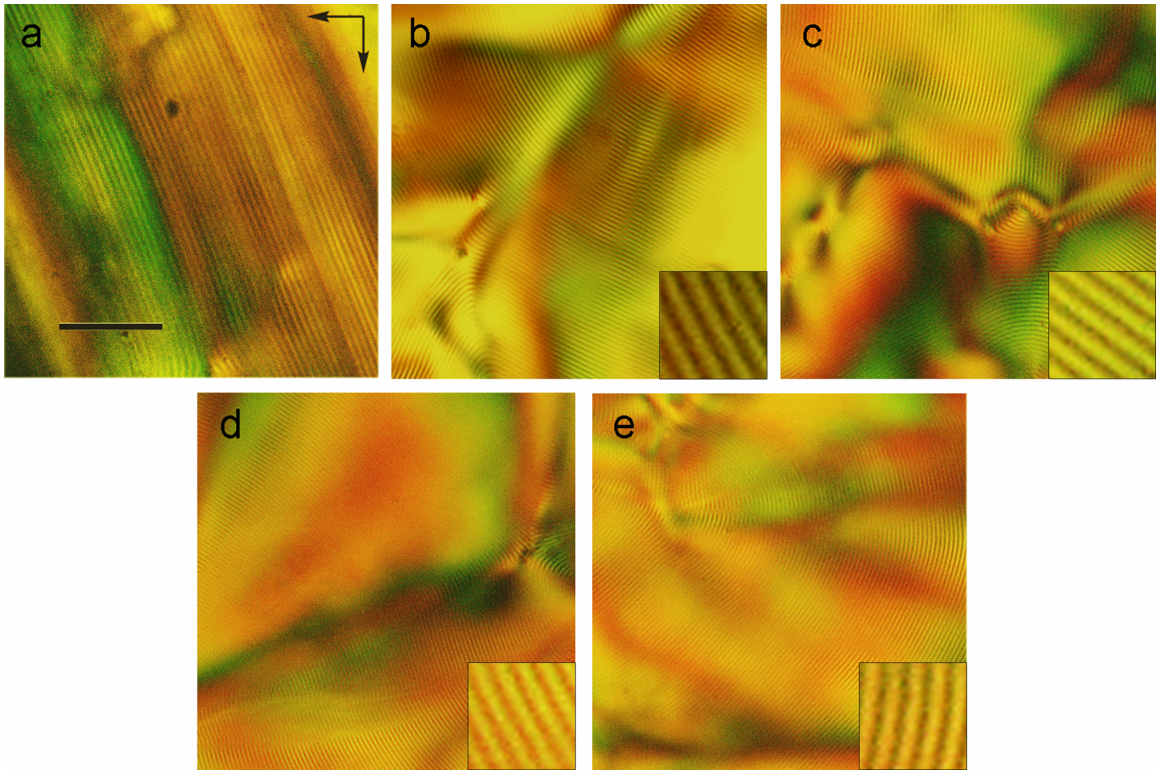


Increase in concentration of a LC film from 30 wt% to 40 wt% of (2'*S*)-(*P*)-**3**-PHIC in toluene, leading to a decrease in pitch length from 6.0 μm to 2.9 μm:



Optical micrograph of a thin film (thickness:200 μm) of (2'*S*)-(*P*)-**3**-PHIC in toluene (40 wt%), p = 2.9 μm. Scalebar, 50 μm. The arrows indicate the directions of the crossed polarizers.

Multiple UV (λ = 365 nm) / visible light (λ >480 nm) irradiation cycles, leading to approximately the same final pitch distance after prolonged visible light (λ >480 nm) irradiation. The final pitches are much shorter than the initial pitch distance obtained before irradiation: 4.0-4.4 μm compared to an initial 6.9 μm:



Optical micrograph of a thin film (thickness: 200 μm) of a) (2'*S*)-(*P*)-**3**-PHIC in toluene (~30 wt%, the concentration is slightly lower than that of the sample used earlier, causing the slightly longer pitch observed, p = 6.9 μm), b) after a first cycle of 1 h of UV (λ = 365 nm) and 20 h of visible light (λ >480 nm) irradiation (p = 4.4 μm), c) after a second (p = 4.1 μm), d) a third (p = 4.0 μm) and e) a fourth irradiation cycle (p = 4.2 μm). Scalebar, 50 μm. The arrows indicate the directions of the crossed polarizers. Insets show a selection under 5x higher magnification.