Electronic Supplementary Material (ESI) for Chemical Science

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Iron oligopyridine complexes as efficient catalysts for practical oxidation of arenes, alkanes, tertiary amines and *N*-acyl cyclic amines with Oxone

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Syntheses and characterizations of 2 and 3.

[Fe(spy)]$_2$(ClO$_4$)$_4$ (2)

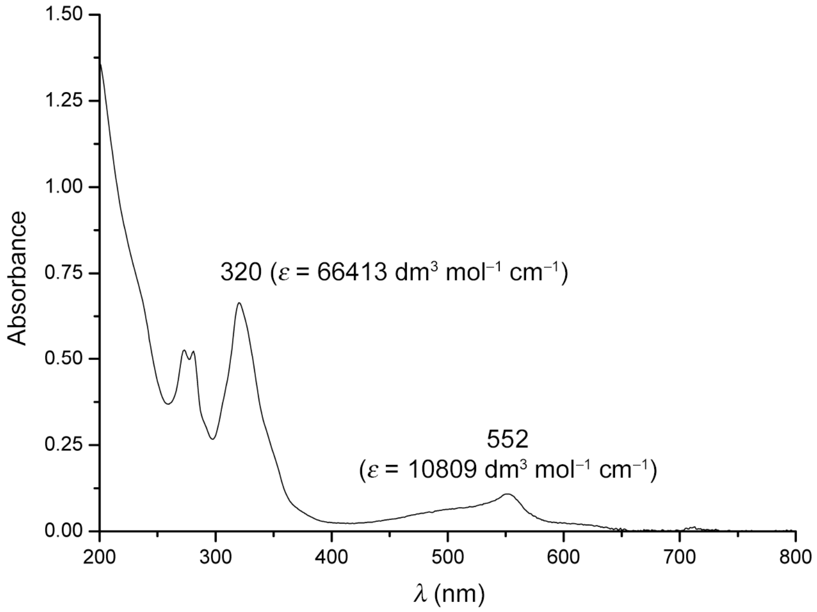
In a 50 mL round bottom flask, spy (4.64 g, 10 mmol) and $Fe(ClO_4)_2 \cdot 6H_2O$ (3.63 g, 10 mmol, 1 equiv.) were dissolved in 30 mL of acetonitrile and the solution was turned to purple immediately. After stirring at room temperature under argon atmosphere for additional 4 h, the solution was filtered by filter paper. Diethyl ether was slowly added to the filtrate and the complex was precipitated from the solution. The product was collected by filtration, washed with diethyl ether and dried under reduced pressure (92% yield). UV/Vis (CH_3CN): λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 552 (10809), 320 (66413). ESI-MS: *m/z* 260.0 ($[Fe_2(spy)_2]^{4+}$). $C_{60}H_{40}Cl_4Fe_2N_{12}O_{16}$ (%) cacld. C: 50.10; H: 2.80; N: 11.68; Found C: 49.48; H: 3.03; N: 11.22.

[Fe(septipy)]$_2$(ClO$_4$)$_4$ (3)

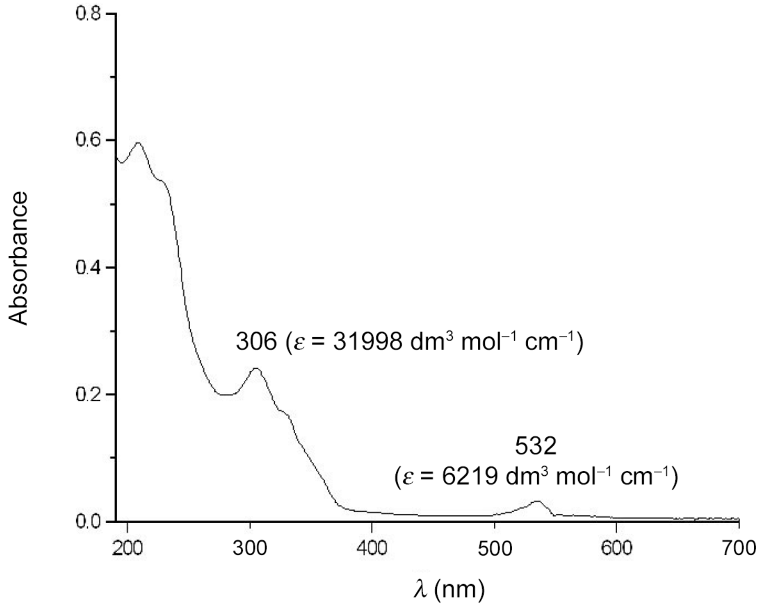
In a 50 mL round bottom flask, septipy (1.08 g, 2 mmol) and $Fe(ClO_4)_2 \cdot 6H_2O$ (726 mg, 2 mmol, 1 equiv.) were dissolved in 5 mL of acetonitrile and the solution was turned to purple immediately. After stirring at room temperature under argon atmosphere for additional 4 h, the solution was filtered by filter paper. Diethyl ether was slowly added to the filtrate and the complex was precipitated from the solution. The product was collected by filtration, washed with diethyl ether and dried under reduced pressure (98% yield). UV/Vis (CH_3CN): λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 532 (6219), 306 (31998). ESI-MS: *m/z* 298.5 ($[Fe(septipy)]^{2+}$). $C_{70}H_{46}Cl_4Fe_2N_{14}O_{16} \bullet H_2O$ (%) cacld. C: 52.20; H: 3.00; N: 12.17; Found C: 51.74; H: 2.91; N: 12.03.

Attempts to isolate $[Fe(qpy)O]^{2+}$ and/or $[Fe(qpy)O_2]^{2+}$

Upon diffusion of diethyl ether to an CH_3CN solution of the reaction mixture [**1** + PhIO in molar ratio of 1: 1.2] at 0 °C, an orange crystalline solid was obtained and its structure was determined to be $\{[Fe(qpy)(H_2O)]_2(\mu\text{-}O)\}(ClO_4)_4$ (CCDC 818979) by X–ray crystallography. The Fe–O–Fe moiety is close to linearity with an angle of 168.7 (3)° (see Fig. S6 shown below). In contrast to $\{[(phen)_2Fe]_2(H_2O)(\mu\text{-}O)\}(ClO_4)_4$ which was reported to be an excellent epoxidation catalyst (see ref. 11 in text), $\{[Fe(qpy)(H_2O)]_2(\mu\text{-}O)\}(ClO_4)_4$ was found to be a poor catalyst for alkene epoxidation by Oxone or PhIO under the similar reaction conditions.

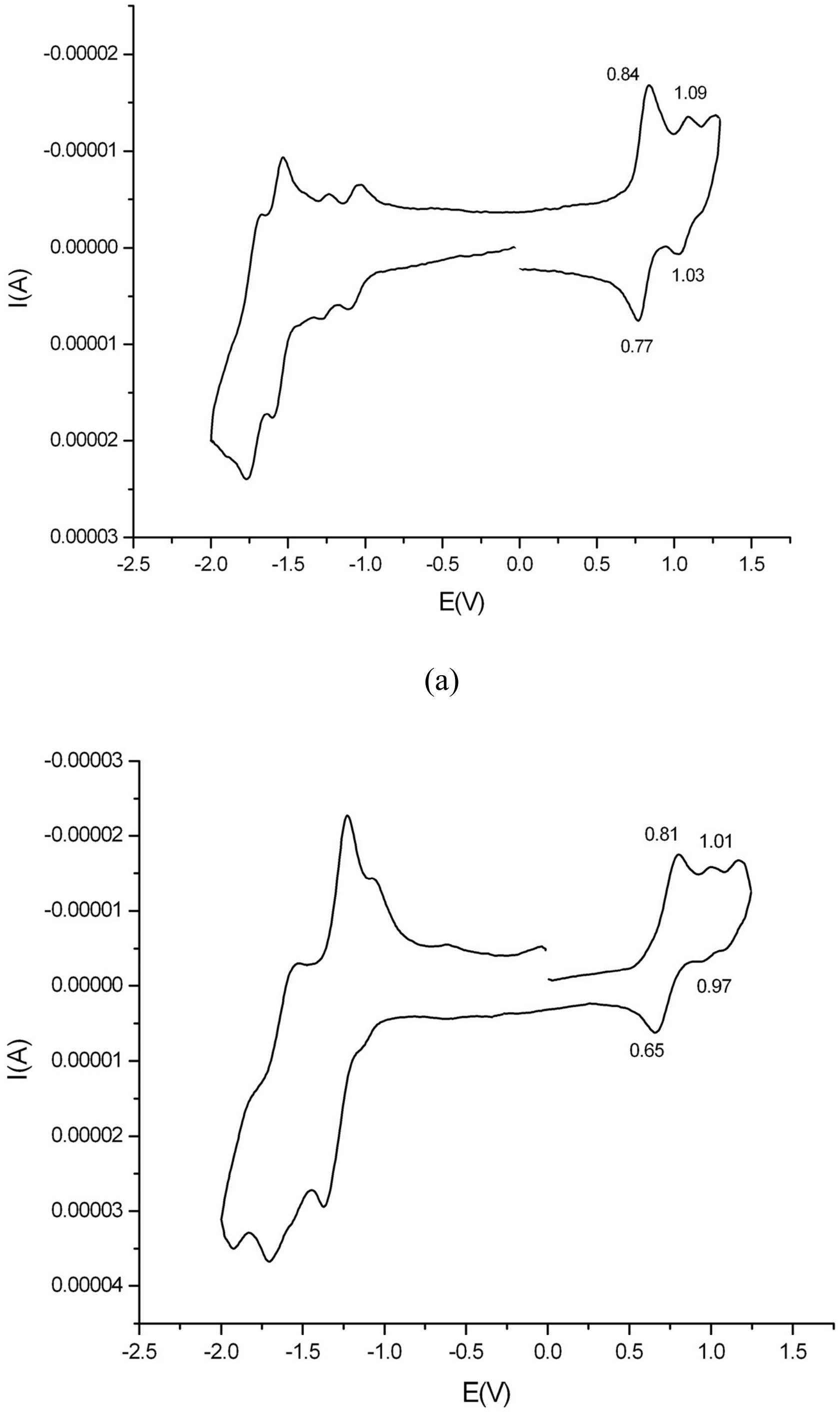


(a)



(b)

Fig. S1 UV-visible absorption spectrum of **2** (a) and **3** (b) in CH_3CN.



(a)

(b)

Fig. S2 Cyclic voltammogram of **2** (a) and **3** (b) in 0.1 M $^{n}Bu_4NPF_6$ CH_3CN solution.

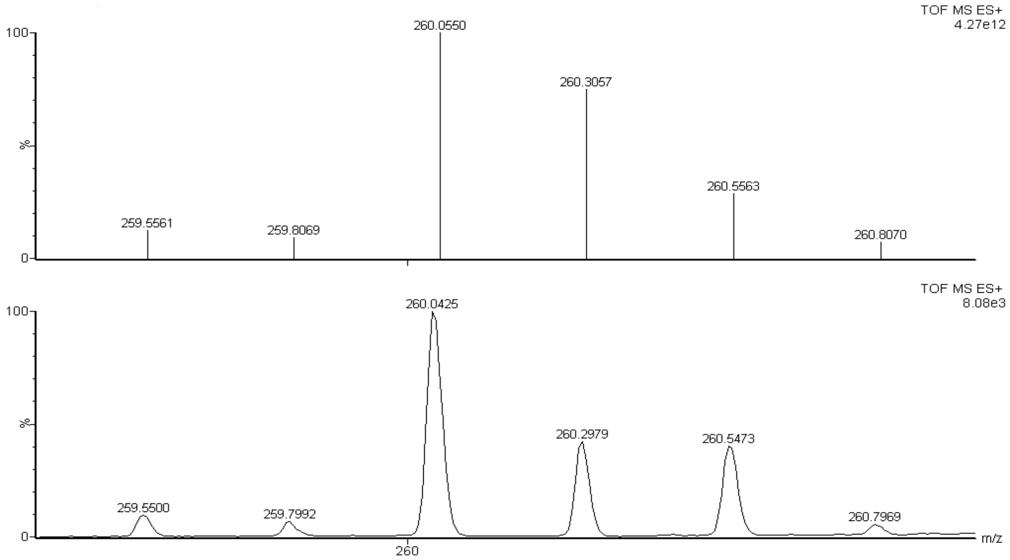


Fig. S3 Electrospray ionization mass spectrum of [$Fe_2(spy)_2](ClO_4)_4$ (**2**) in CH_3CN; simulated isotope pattern ([$C_{60}N_{12}H_{36}Fe_2]^{4+}$, top) and observed isotope pattern (bottom).

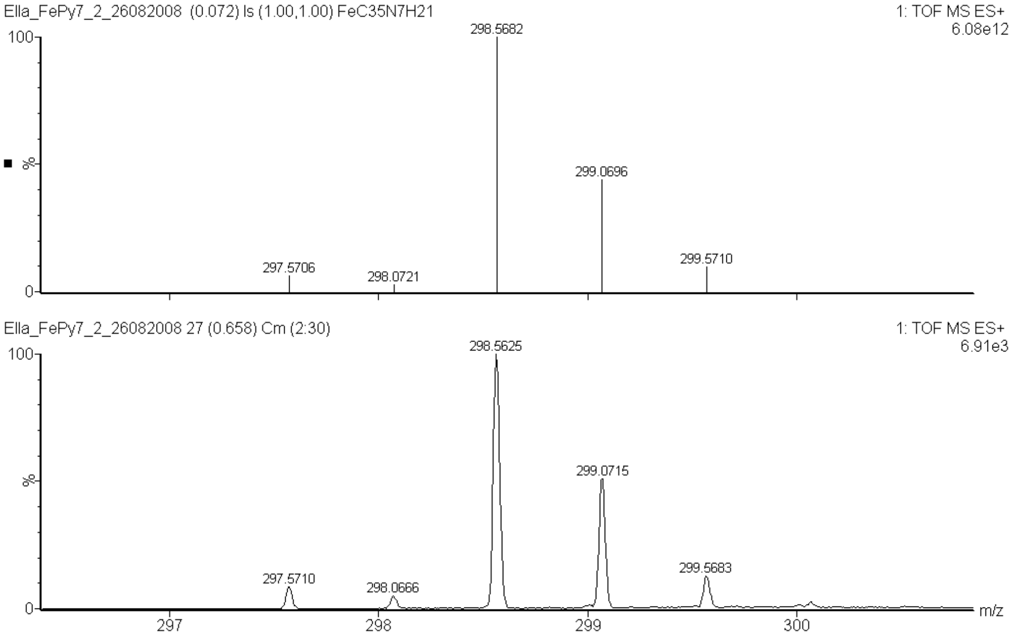
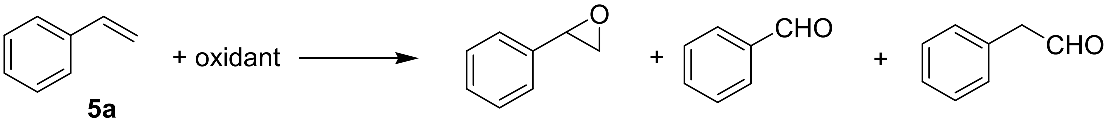
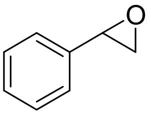
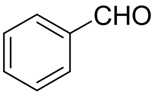
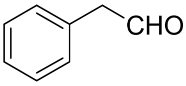


Fig. S4 Electrospray ionization mass spectrum of [$Fe_2(septipy)_2](ClO_4)_4$ (**3**) in CH_3CN; simulated isotope pattern ([$C_{35}N_7H_{21}Fe]^{2+}$, top) and observed isotope pattern (bottom).

Table S1 Oxidation of styene with different oxidants catalysed by **1**.[a,b]



5a

entry	oxidant	conv. [%][c]	yield [%][c]		
					
1	H_2O_2	16	28	11	3
2	H_2O_2 + CH_3COOH	14	33	42	6
3	H_2O_2 + NH_4HCO_3	18	46	11	2
4	$PhI(OAc)_2$	12	81	6	3
5	PhIO	62	91	2	0
6	Oxone	62	16	31	26
7	Oxone + NH_4HCO_3	92	89	2	0

[a] The controlled experiment of using “$Fe(ClO_4)_2$•$6H_2O$ + Oxone” and “NH_4HCO_3 + Oxone” gave poor yields of styrene oxide with low substrate conversion. [c] Substrate/catalyst/oxidant molar ratio = 1/0.05/1.3, room temperature, 2 h. [c] Determined by GC analysis.

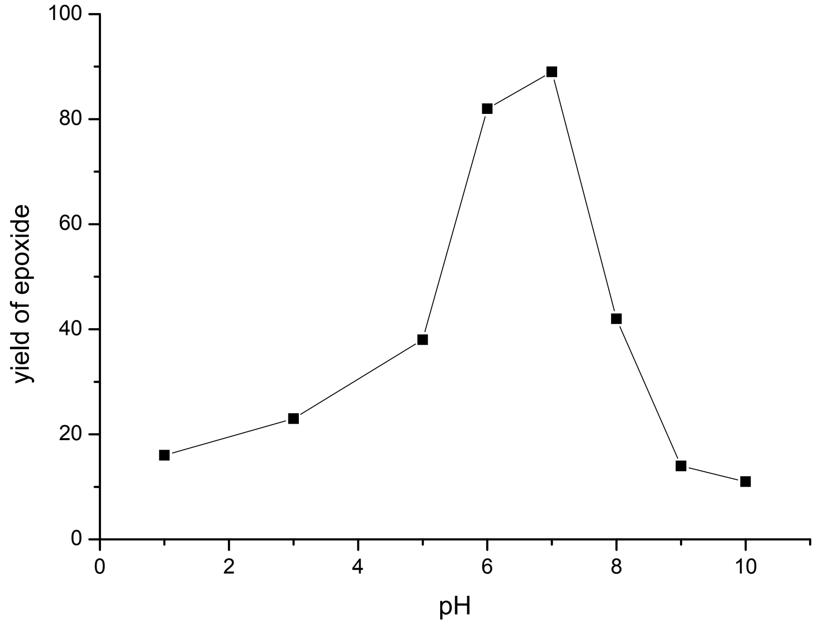


Fig. S5 Epoxidation of styrene (**5a**) using Oxone as terminal oxidant with **1** as catalyst at various pH.

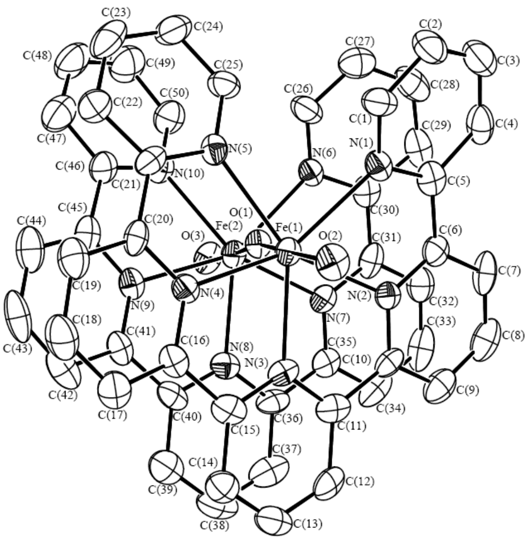
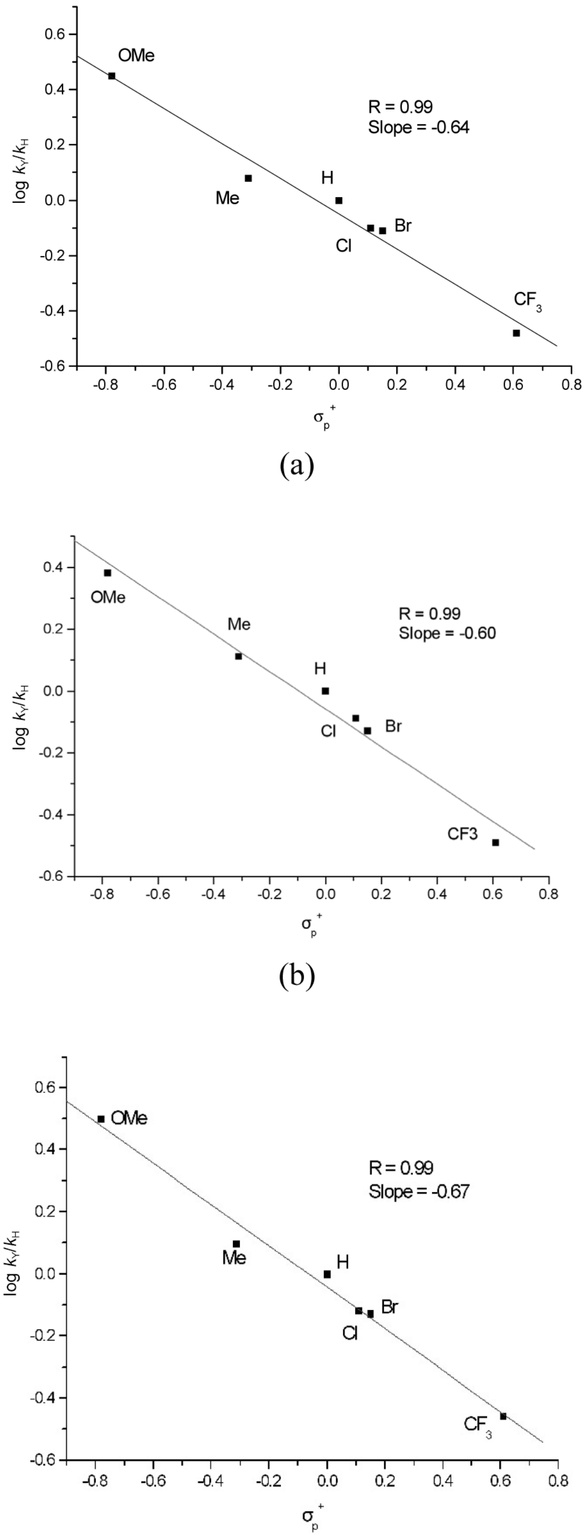


Fig. S6 Perspective view of the complex cation of $\{[Fe(qpy)(H_2O)]_2(\mu\text{-}O)\}(ClO_4)_4$ (hydrogen atoms are not shown).

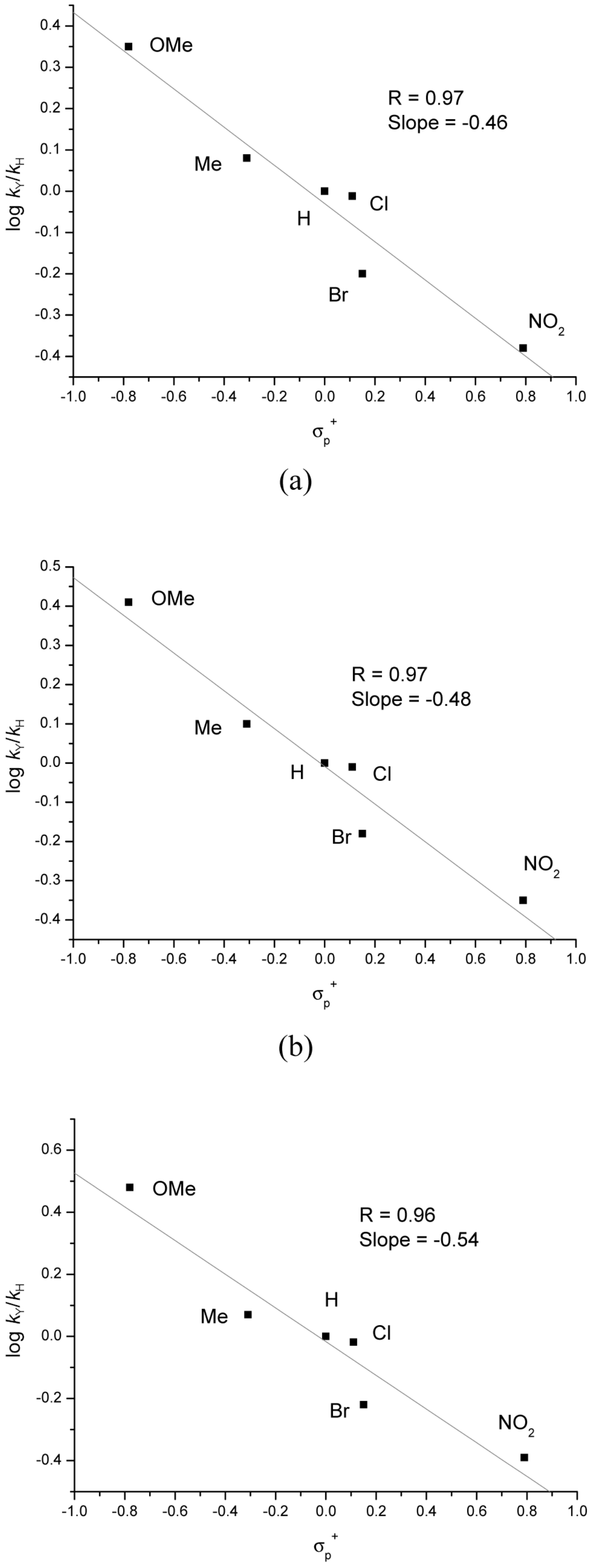


(a)

(b)

(c)

Fig. S7 Plots of log k_Y/k_H vs σ_p^+ for the epoxidation of *para*-substituted styrenes catalysed by **1** (a), **2** (b) and **3** (c).



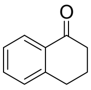
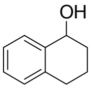
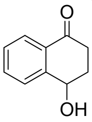
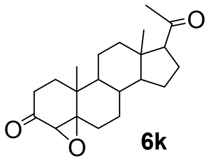
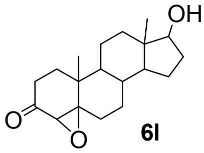
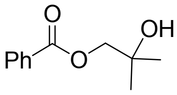
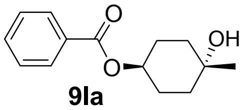
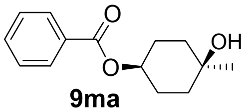
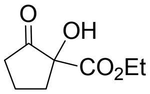
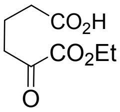
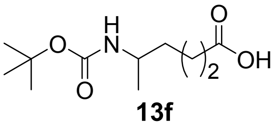
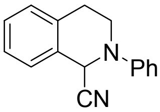
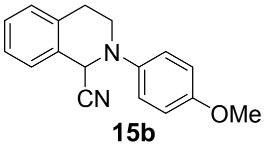
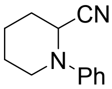
(a)

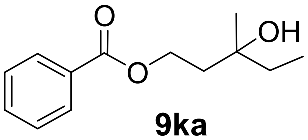
(b)

(c)

Figure S8 Plots of log k_Y/k_H vs σ_p^+ for oxidation of ethyl benzenes catalysed by **1** (a), **2** (b) and **3** (c).

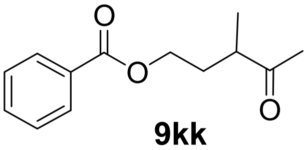
Reported compounds in literature

Compounds	References
6a-g, **6m**, **8a-g**, the products of **9a-i**, **11a-f**, **13a-e**, **13g**, **13h**, **15d-g**, , , ,	Commercially available.
6ha, **6hb**, **6i**, **6j**, **6n**, **6o**,	P. Liu, et al, *Org. Lett.,* 2008, **10**, 3275.
 **6k**	P. Bovicelli, et al, *J. Org. Chem.,* 1992, **57**, 2182.
 **6l**	R. Kluge, *Tetrahedron,* 1996, **52**, 2957.
 **9ja**	G. Reginato, et al, *J. Org. Chem.,* 1990, **55**, 5132.
 **9la**	C. Cianetti, et al, *Tetrahedron*, 1983, **39**, 657.
 **9ma**	C. Cianetti, et al, *Tetrahedron,* 1983, **39**, 657.
 **9na**	J. Christoffers, *J. Org. Chem.,* 1999, **64**, 7668.
 **9nk**	J. N. Payette, et al, *J. Am. Chem. Soc.*, 2008, **130**, 12276.
 **13f**	R. Ito, et al, *J. Am. Chem. Soc.,* 2005, **127**, 834.
 **15a**	S.-I. Murahashi, et al, *J. Am. Chem. Soc.,* 2003, **125**, 15312.
 **15b**	W. Han, et al, *Chem. Commun.,* 2009, 5024.
 **15c**	S.-I. Murahashi, et al, *Angew. Chem., In. Ed.,* 2005, **44**, 6931.



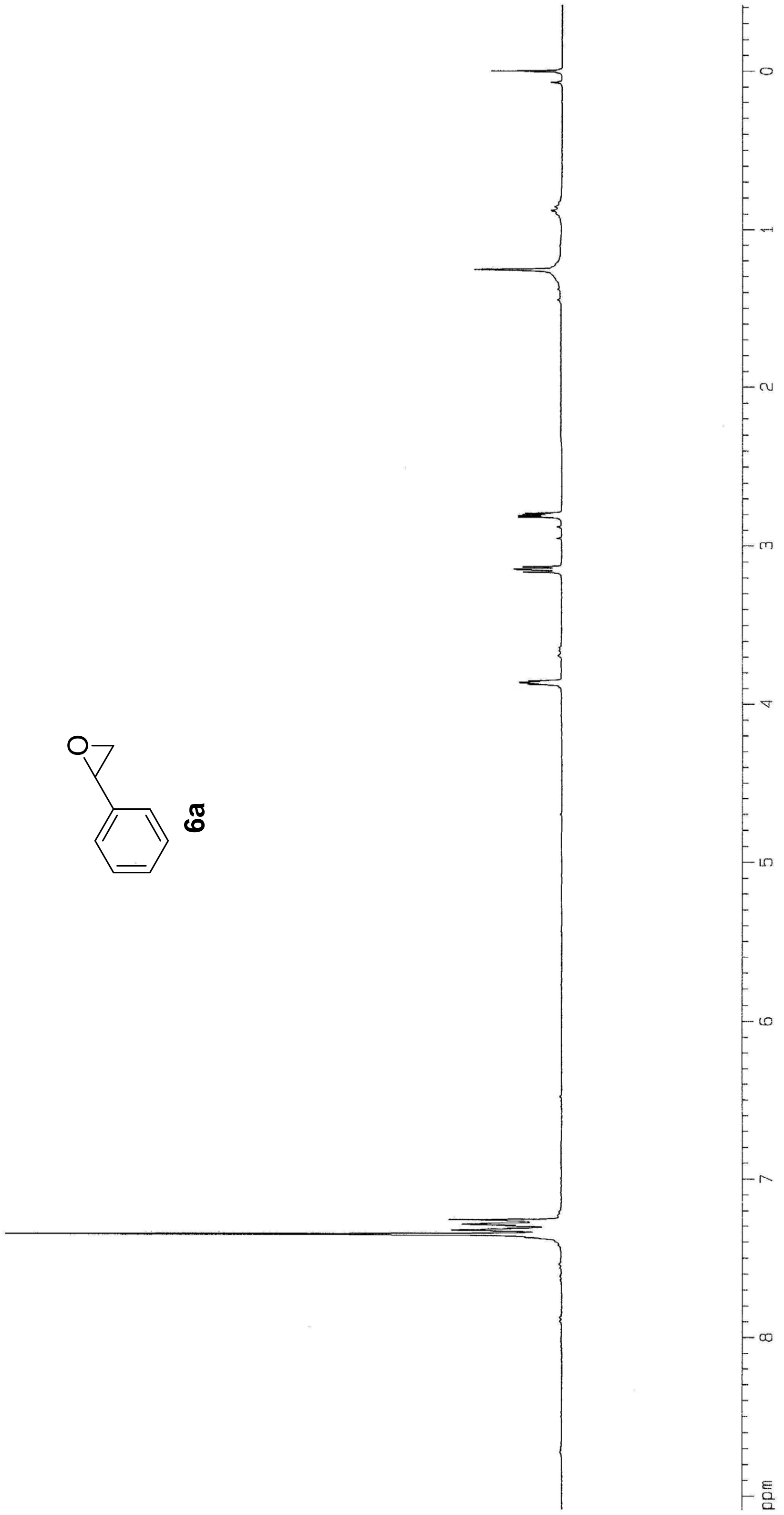
9ka

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.14 (d, *J* = 8.1 Hz, 2H), 7.61 (m, 1H), 7.48 (m, 2H), 4.50 (t, *J* = 6.9 Hz, 2H), 1.96 (m, 2H), 1.58(q, *J* = 7.5 Hz, 2H), 1.27 (s, 3H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.65, 132.95, 129.53, 128.41, 72.16, 61.80, 39.37, 35.02, 26.61, 8.26. MS (EI) *m/z* 204 ([M-H$_2$O]$^+$); HRMS (EI) *m/z* for $C_{13}H_{16}O_2$ ([M-H$_2$O]$^+$) calcd 204.1150, found 204.1143.



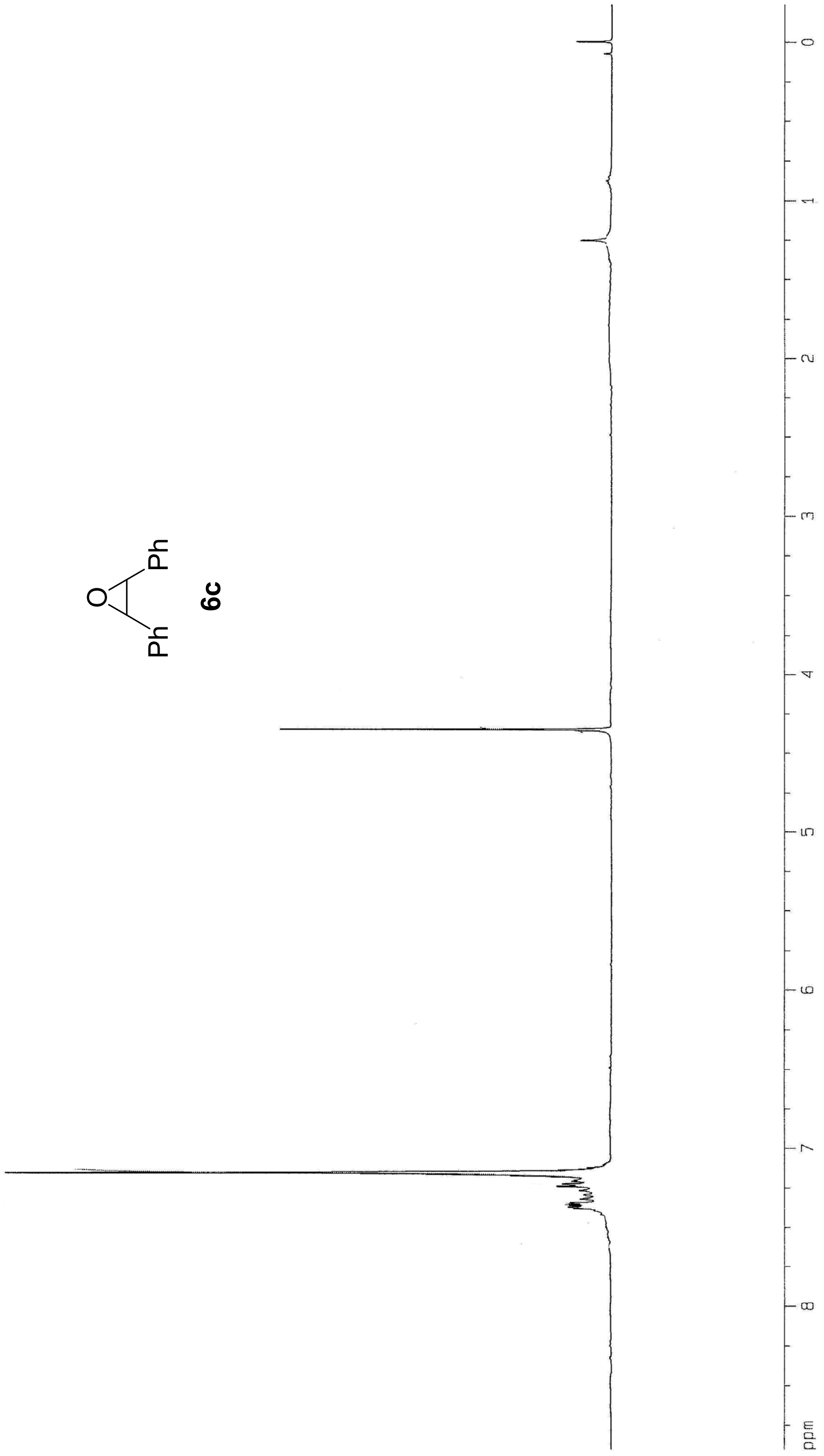
9kk

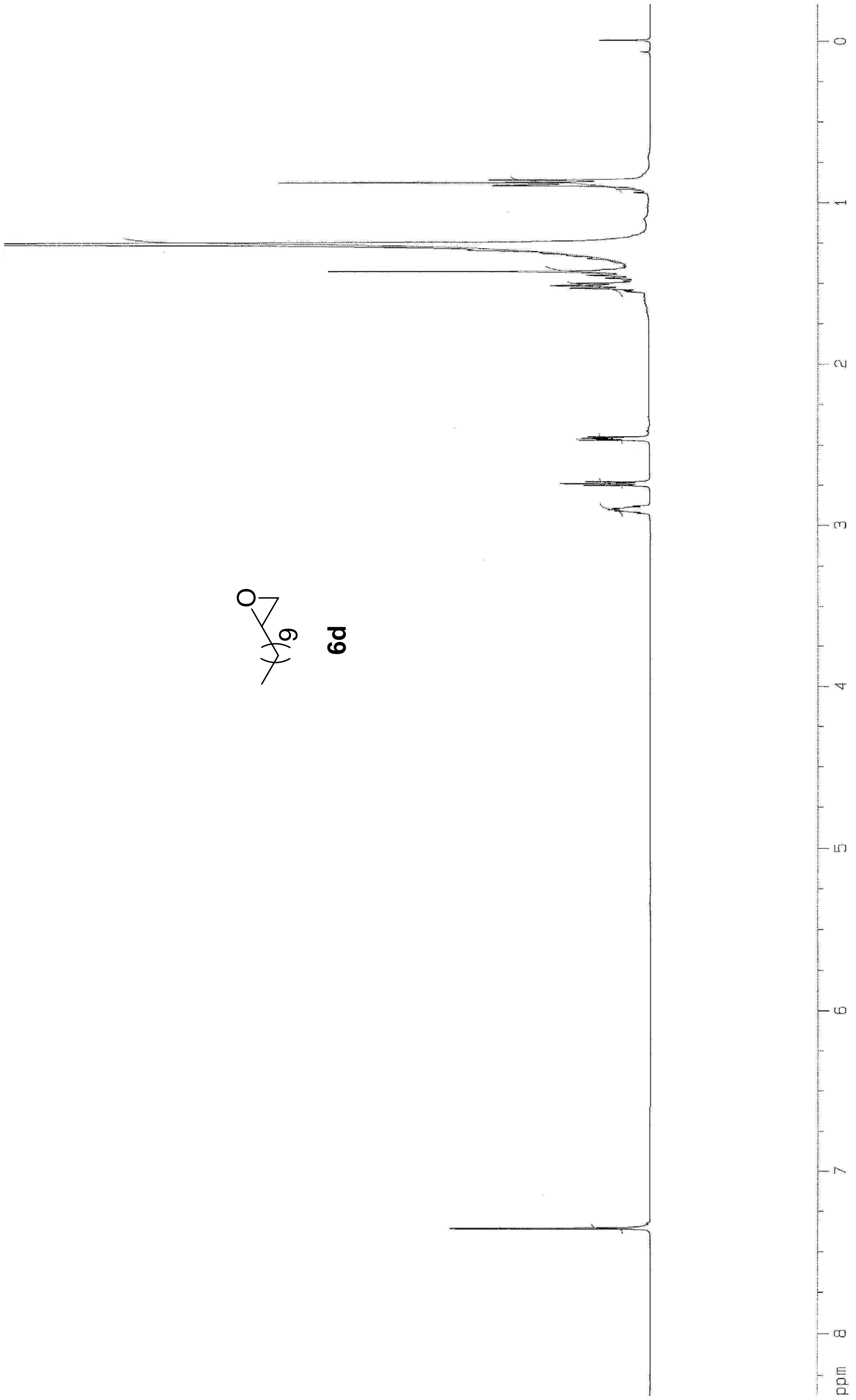
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.56 (m, 1H), 7.45 (m, 2H), 4.34 (t, *J* = 6.4 Hz, 2H), 2.73 (m, 1H), 2.19 (m, 1H), 2.18 (s, 3H), 1.78 (m, 1H), 1.19 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 211.49, 166.53, 133.01, 129.56, 128.42, 62.93, 43.99, 31.49, 28.4, 16.57. MS (EI) *m/z* 220 (M$^+$); HRMS (EI) *m/z* for $C_{13}H_{16}O_3$ (M$^+$) calcd 220.1099, found 220.1094.



6a

6c





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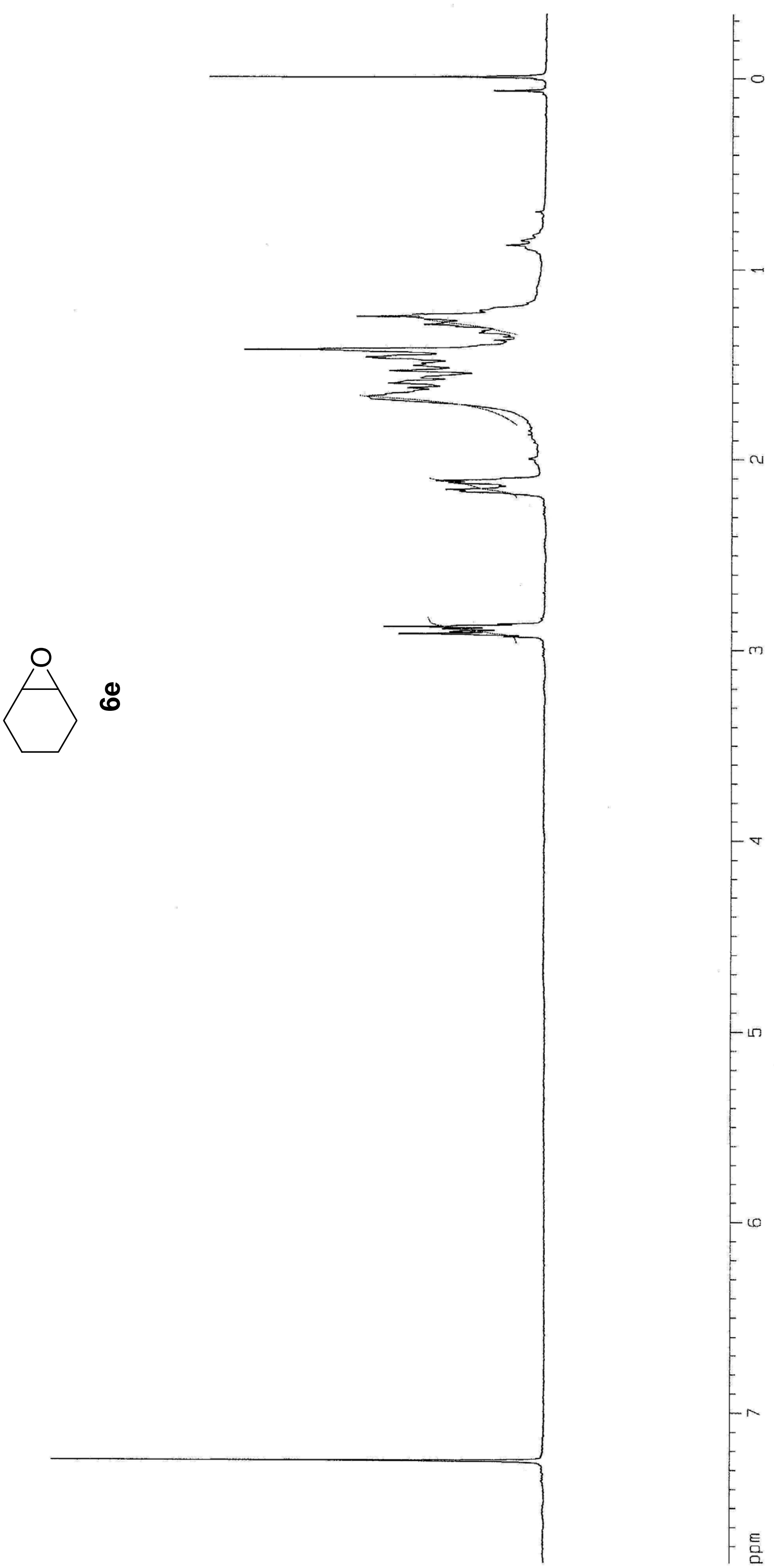

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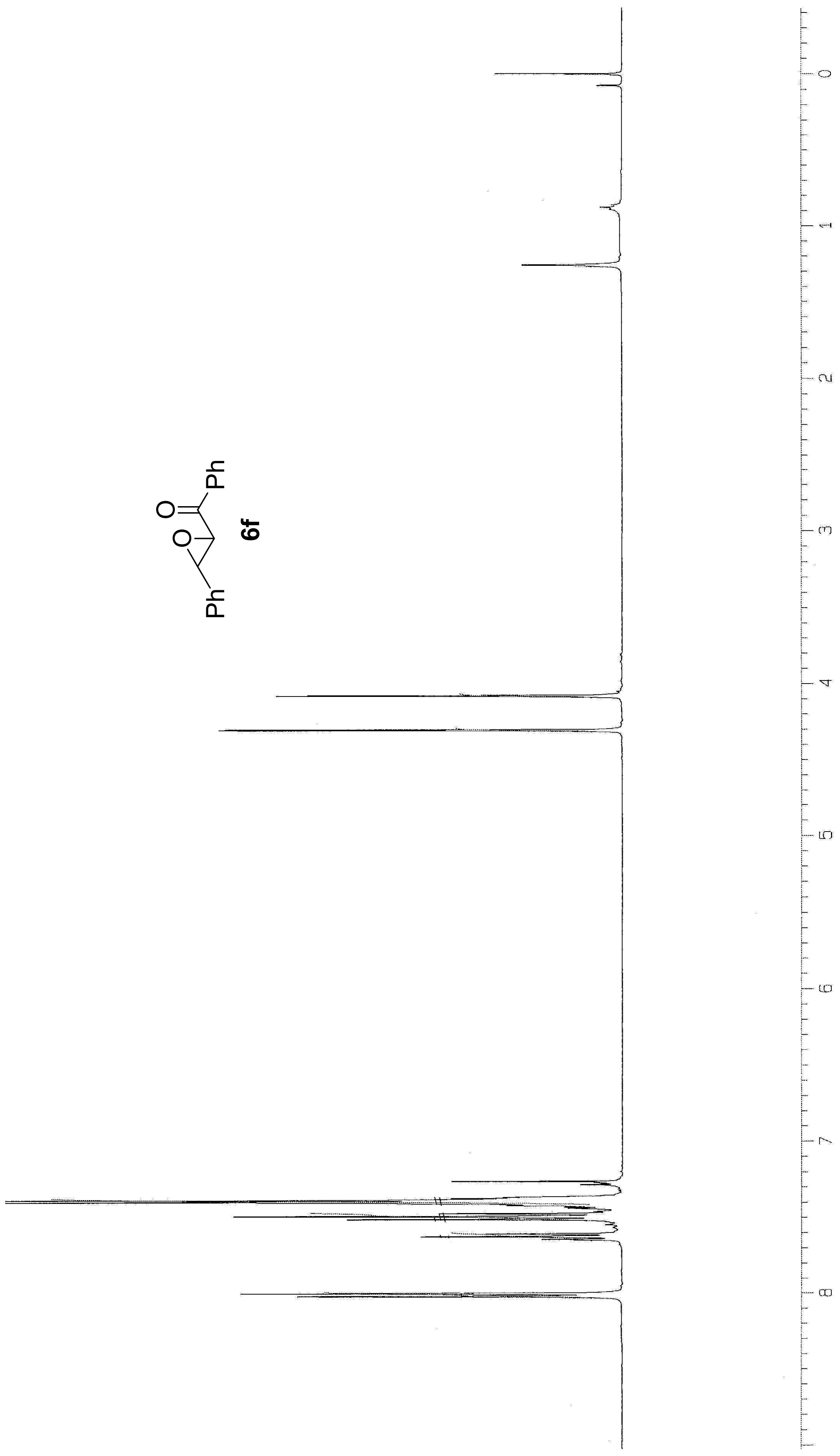
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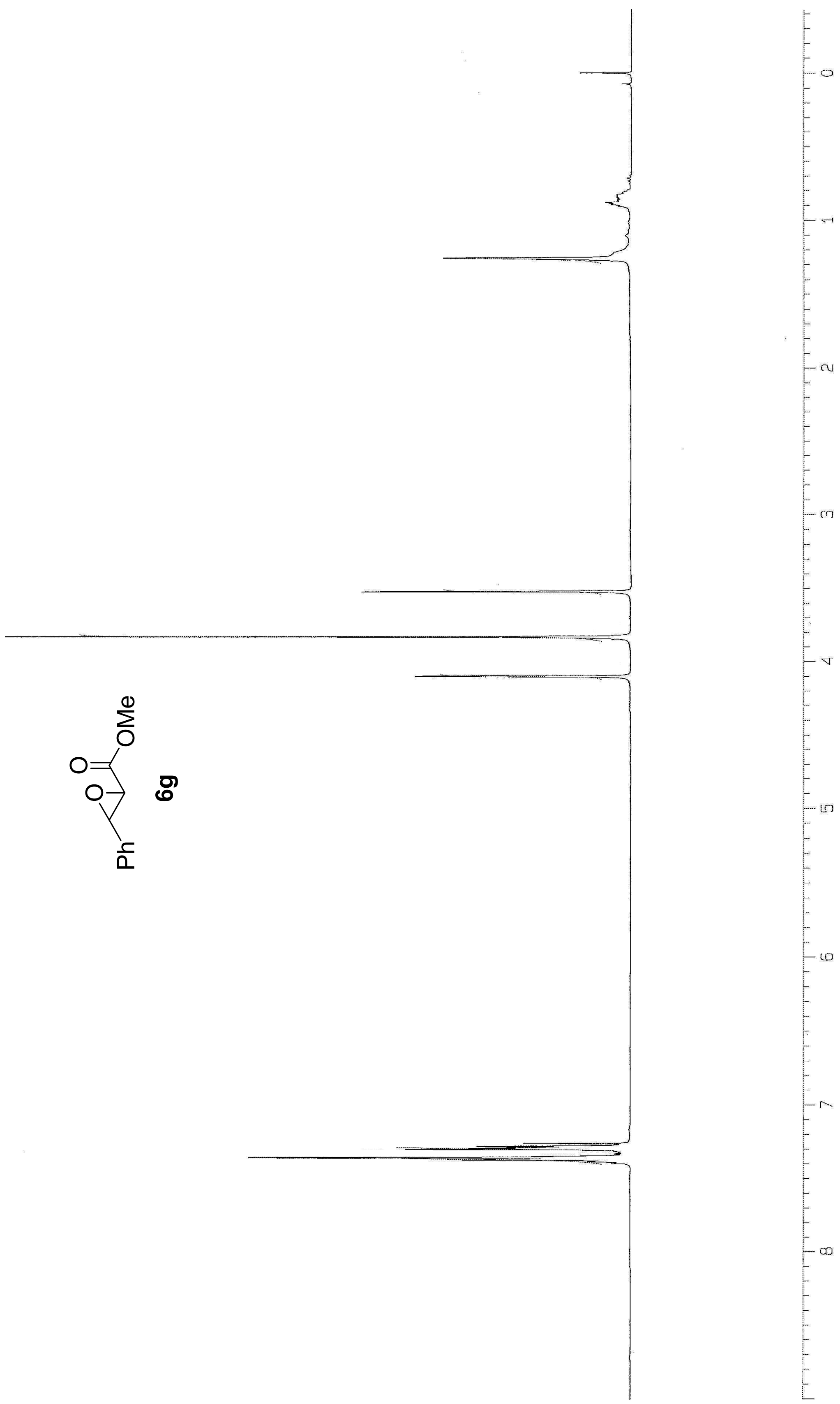
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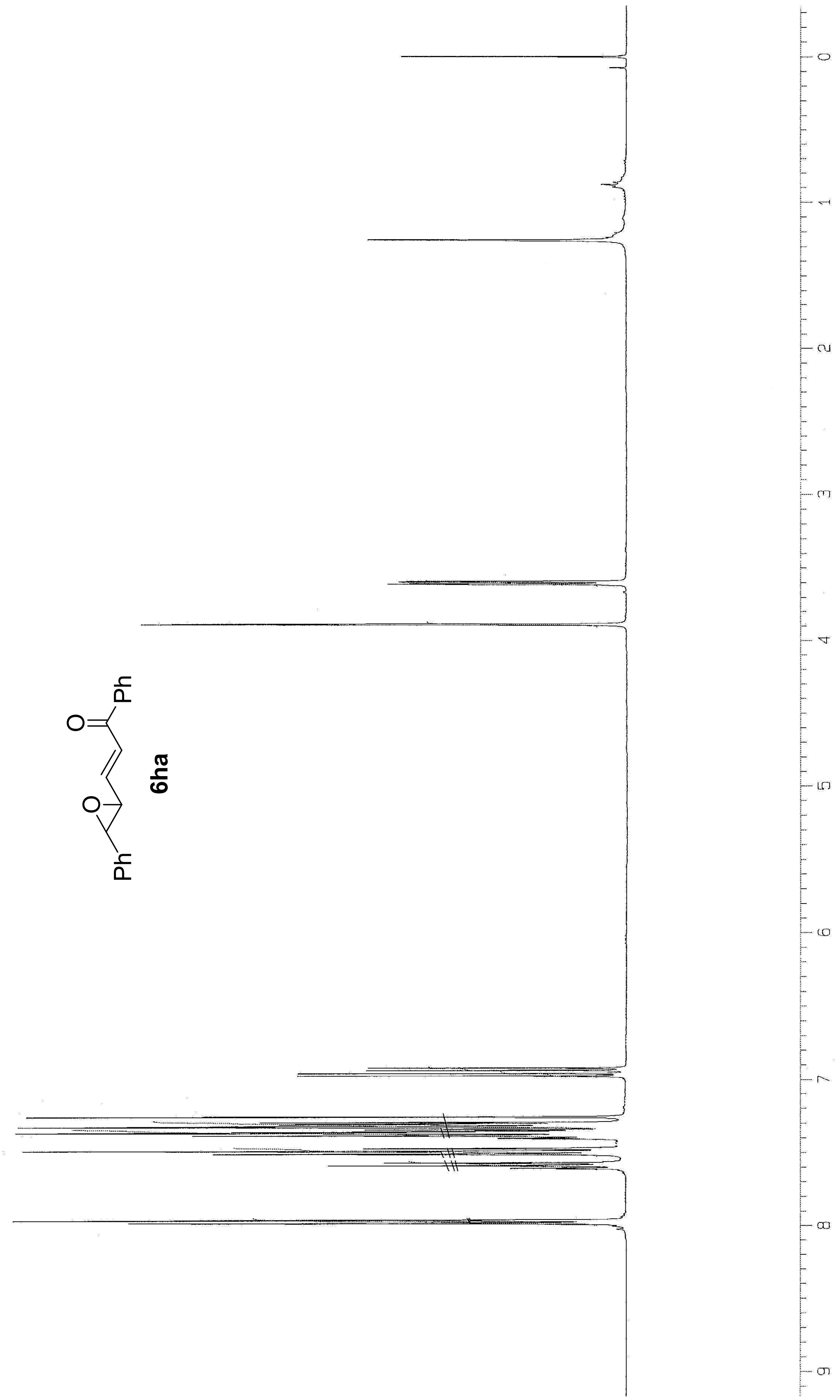

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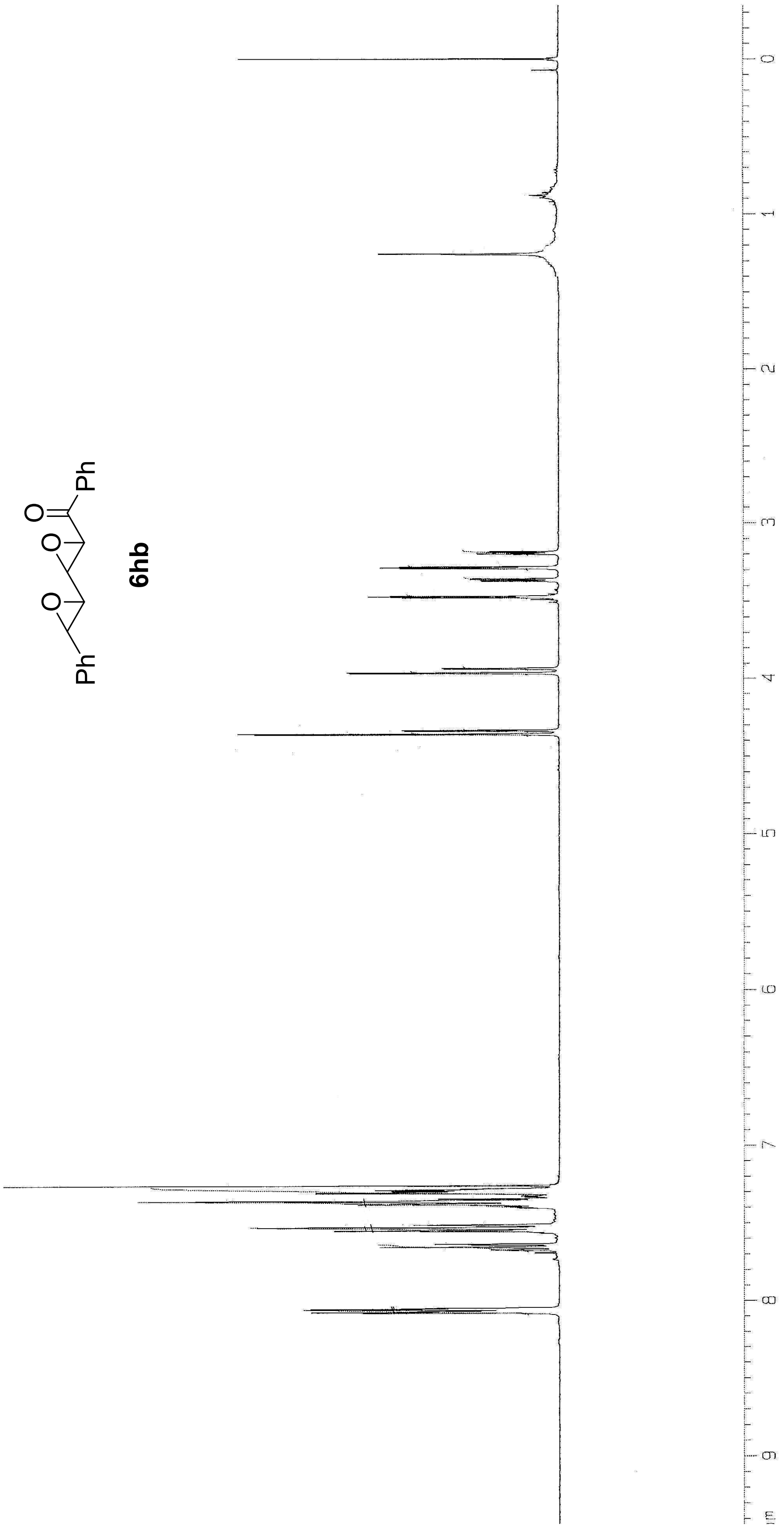

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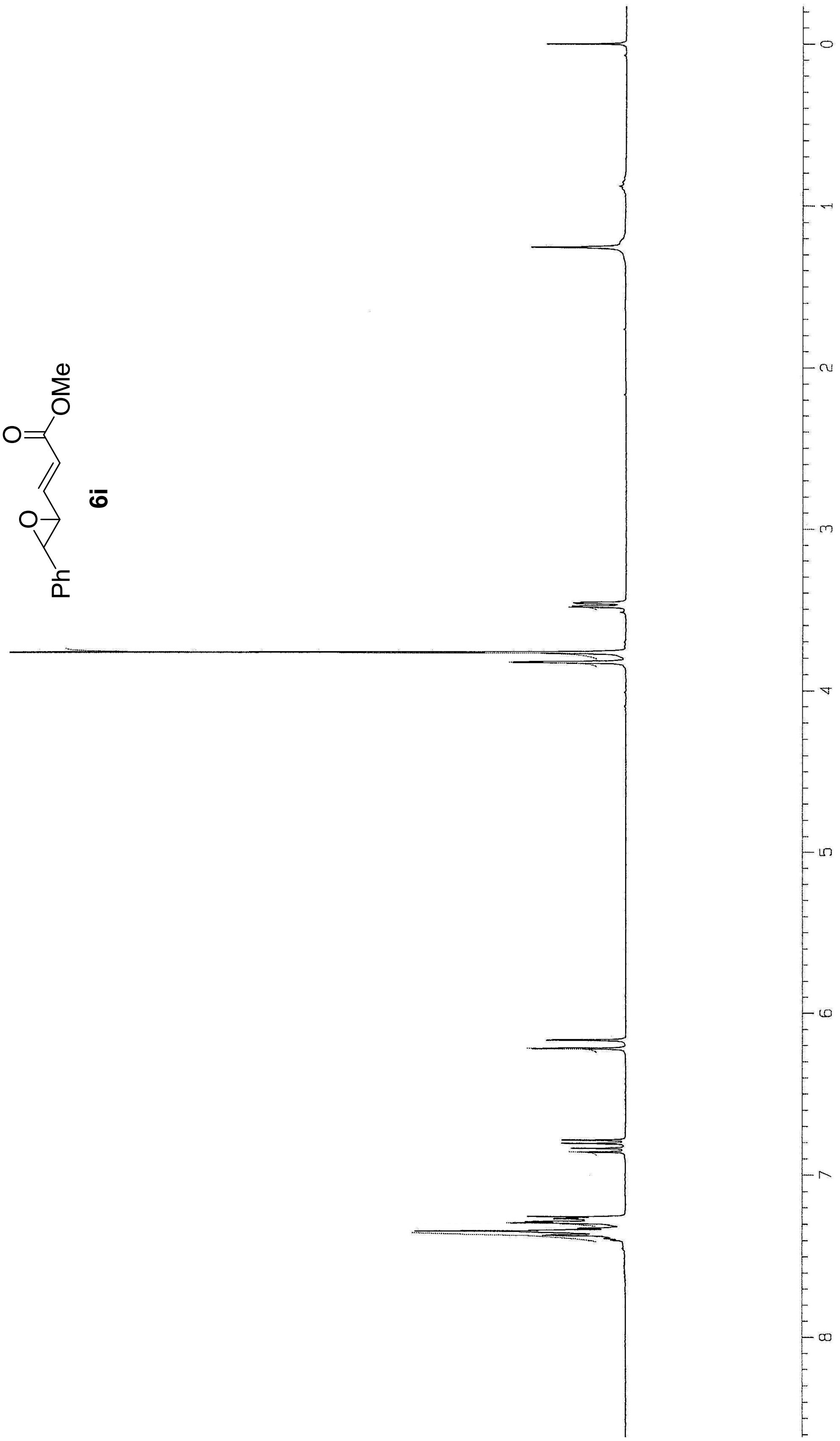

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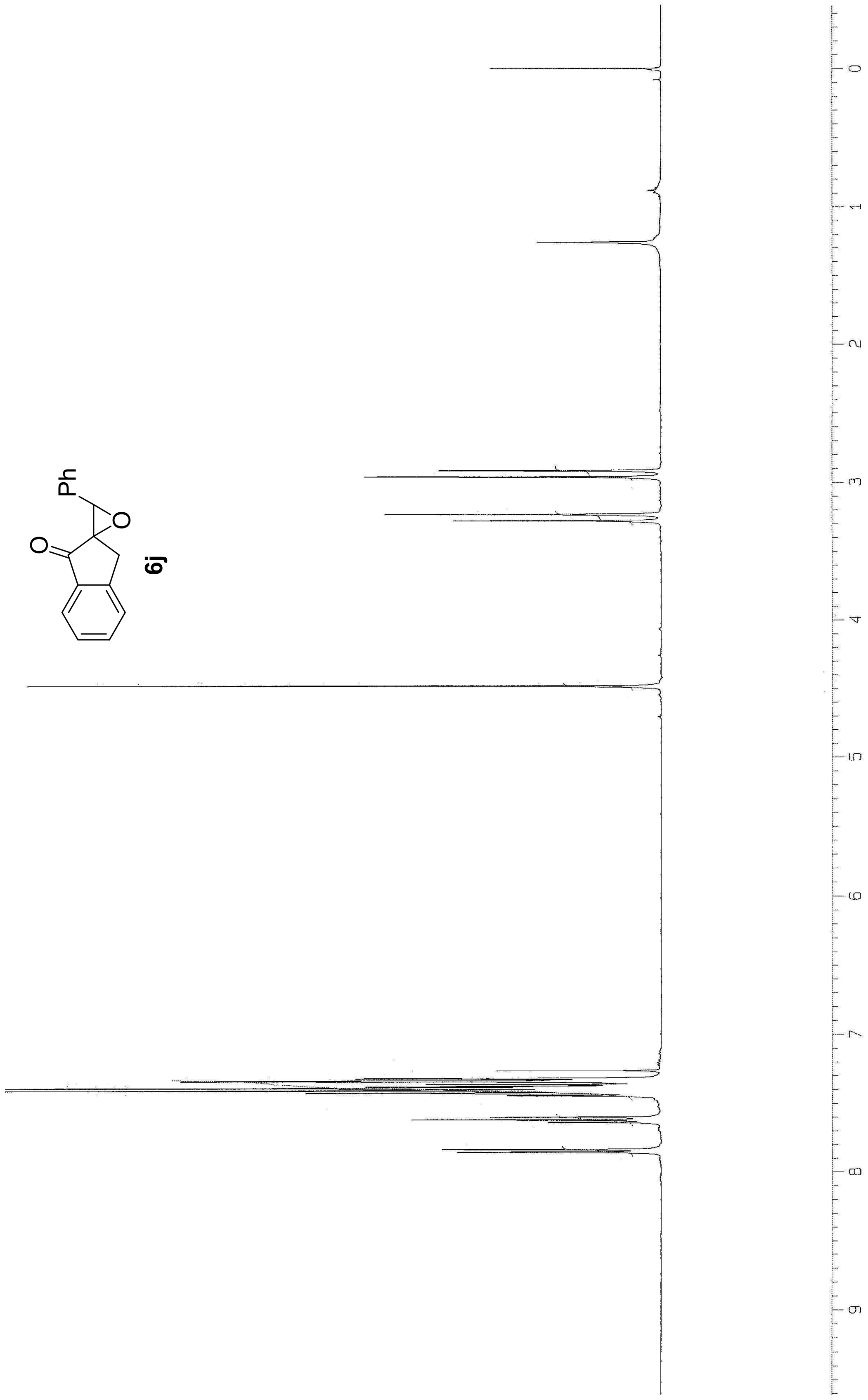

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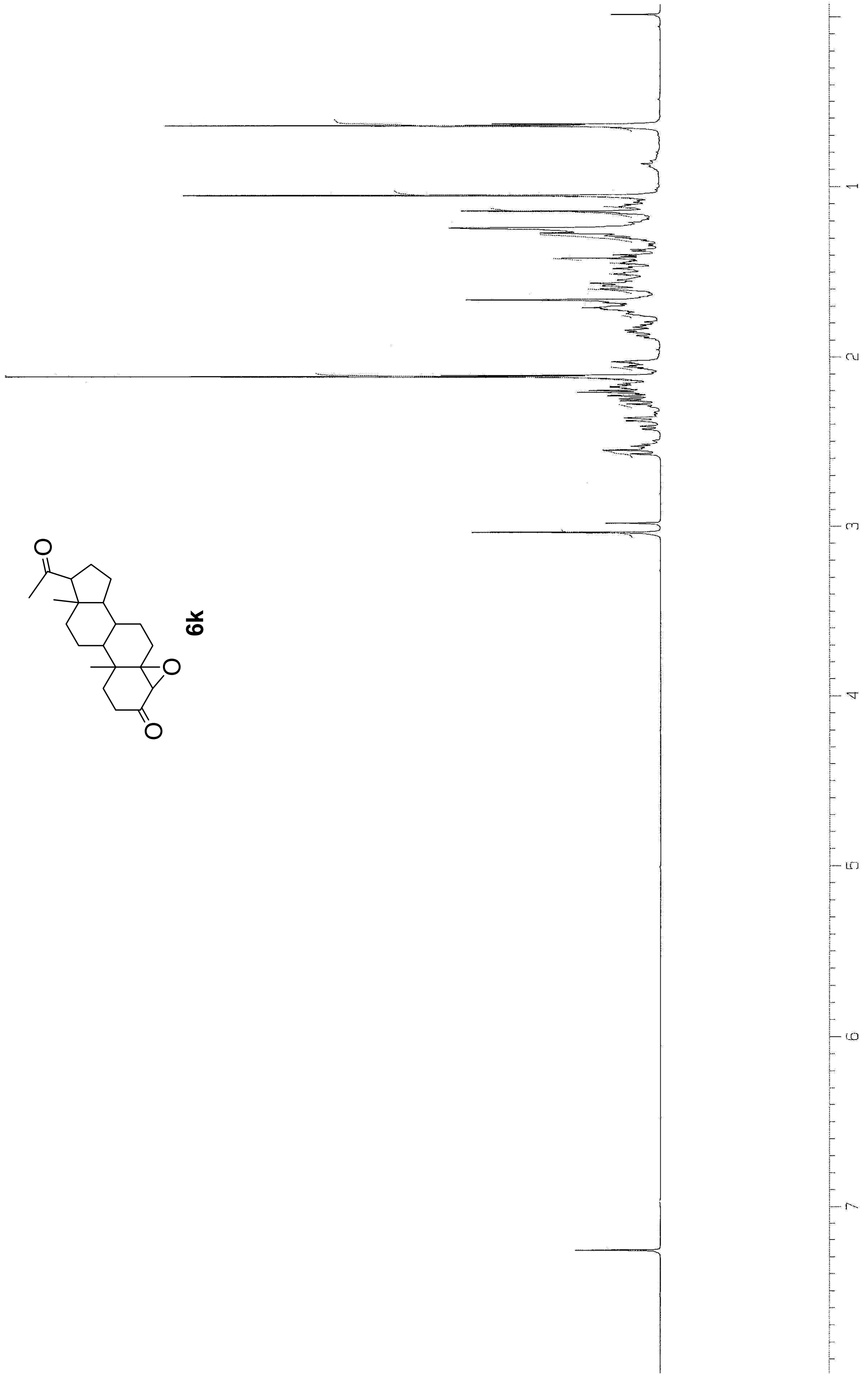

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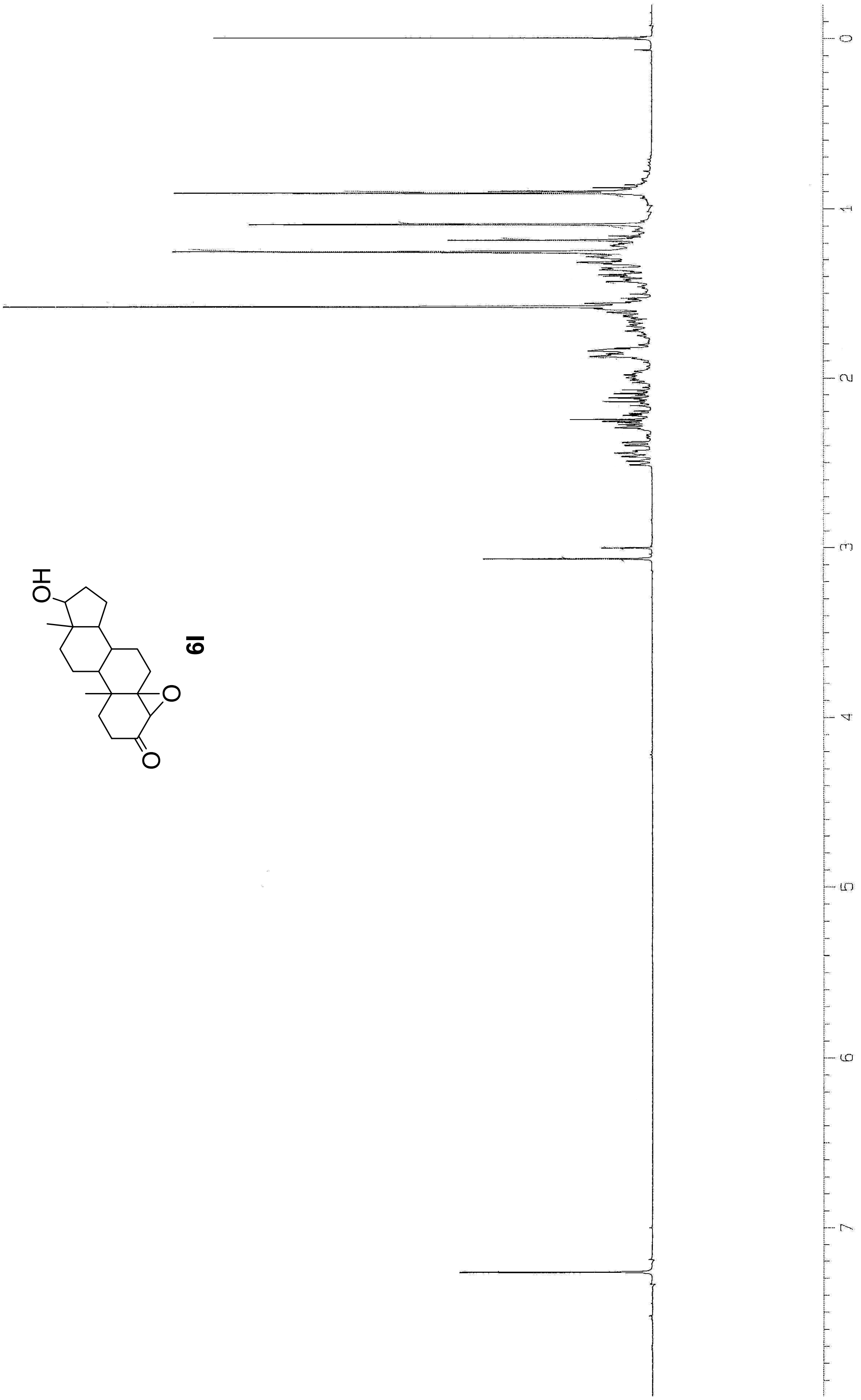

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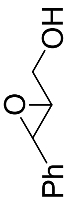

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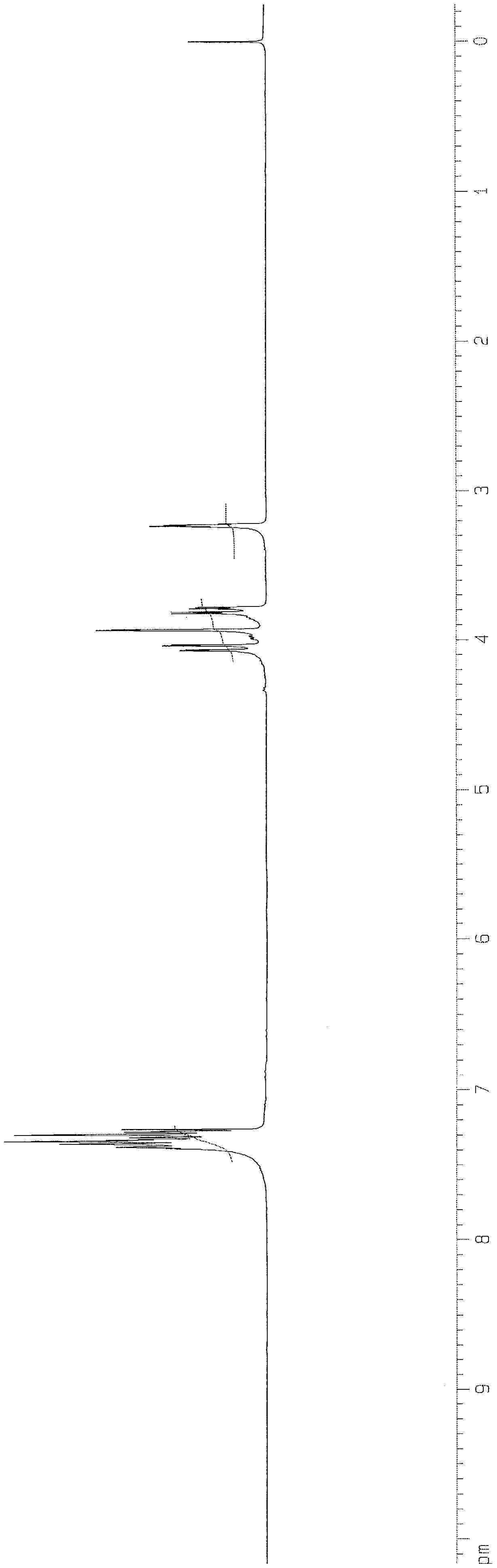

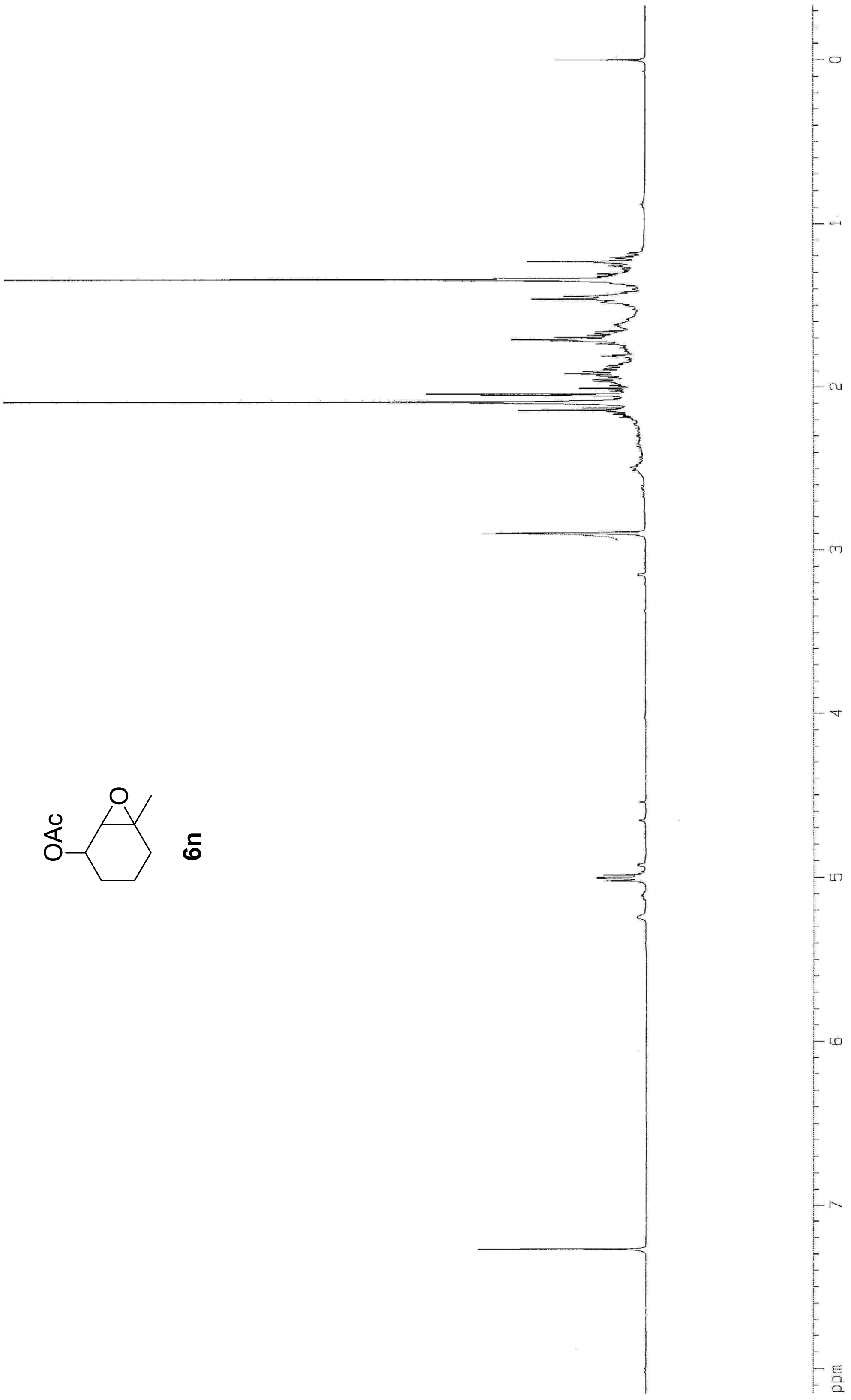

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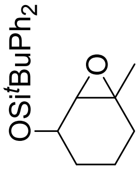

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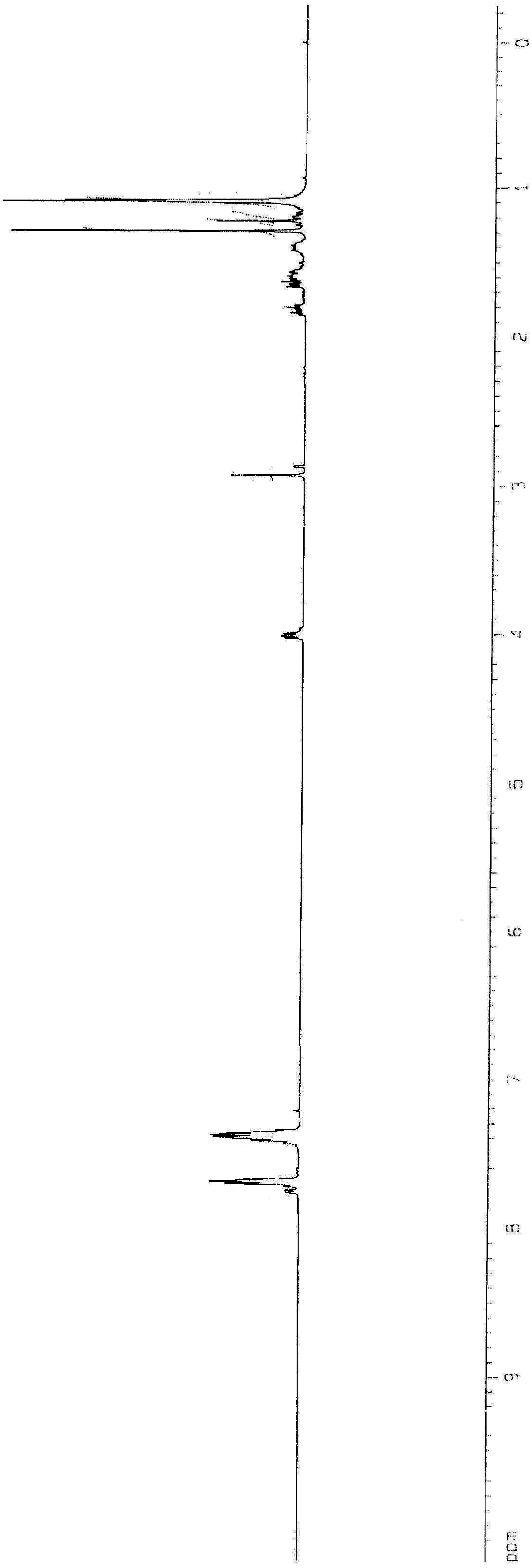

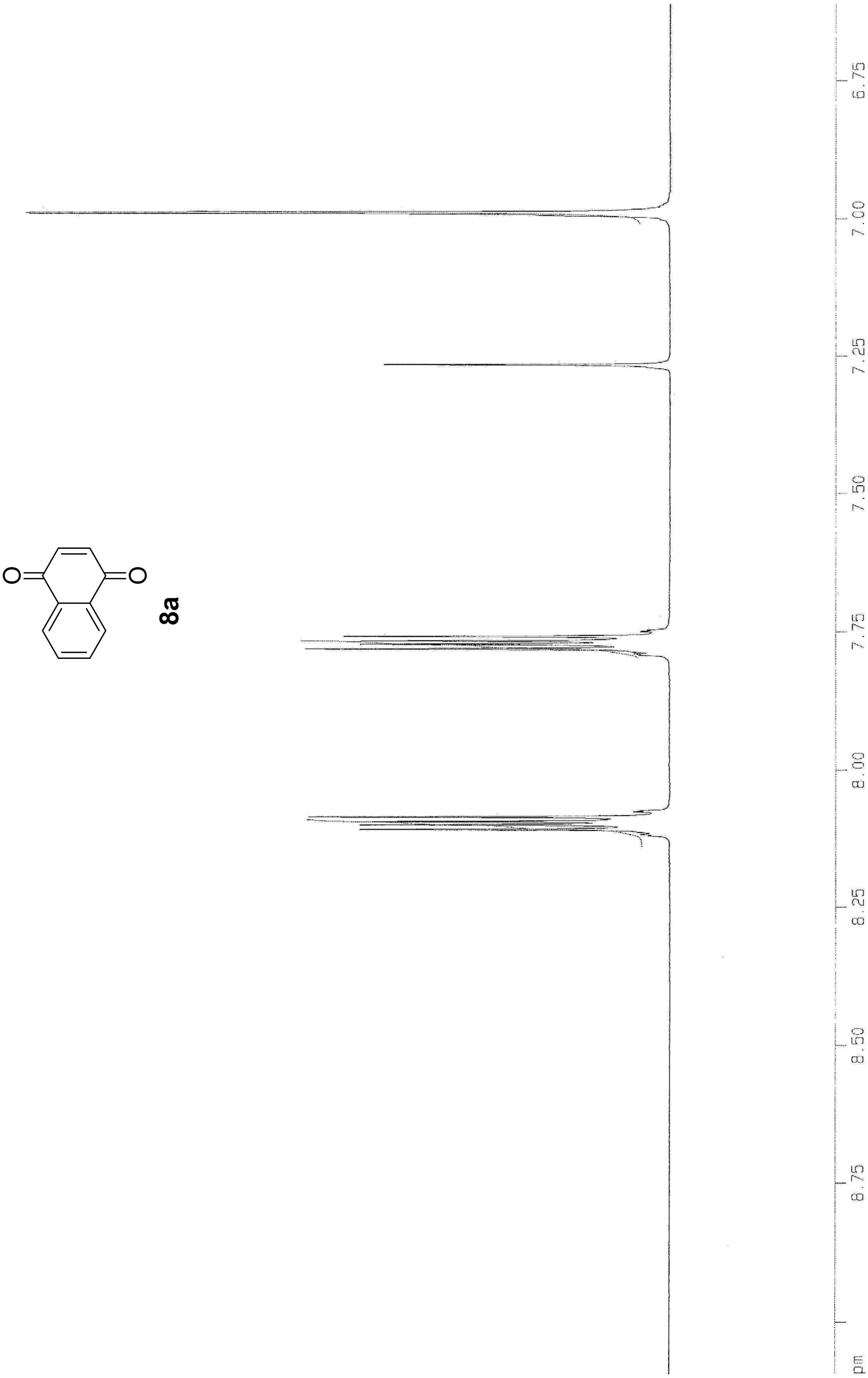

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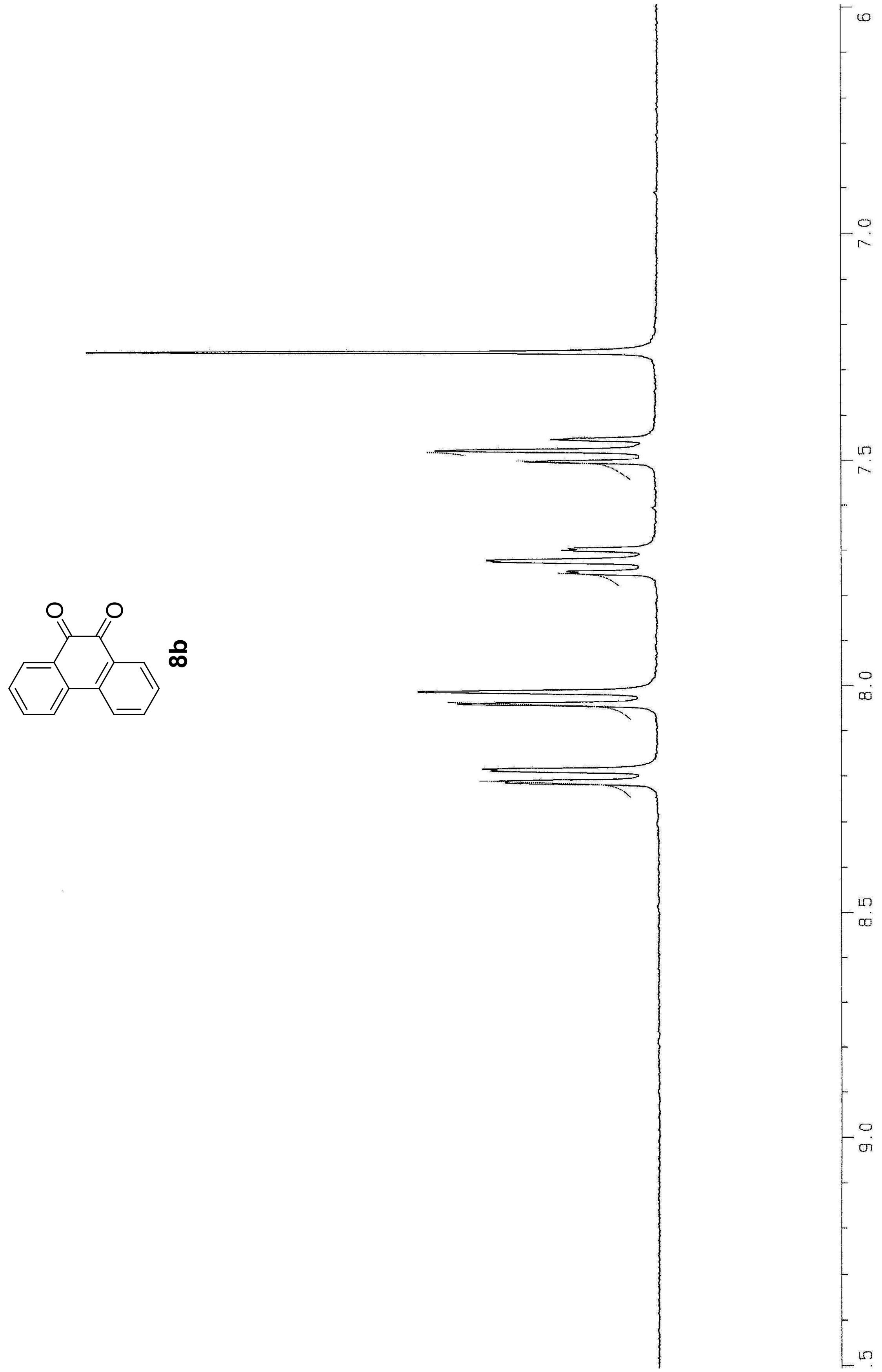
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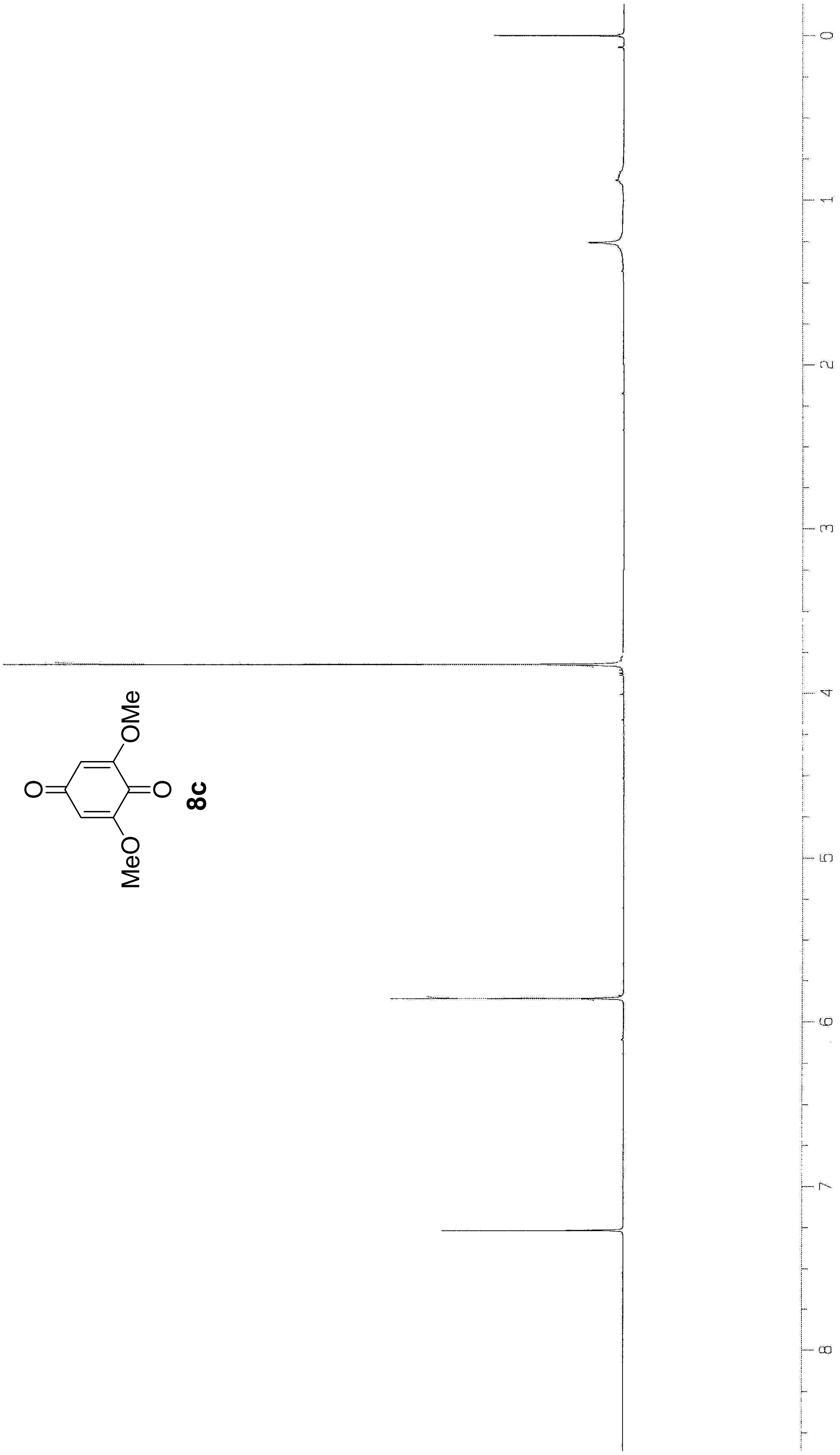

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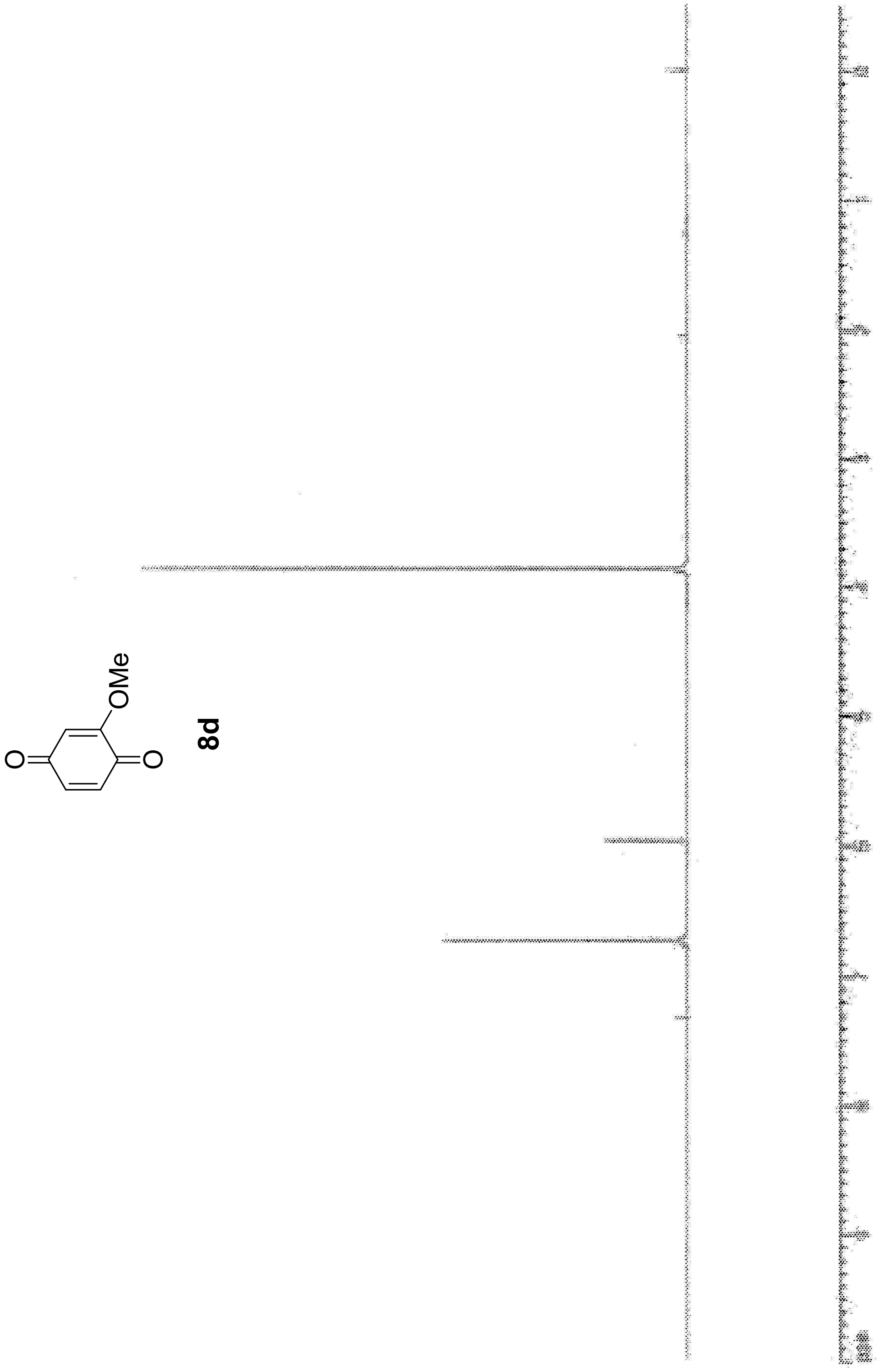

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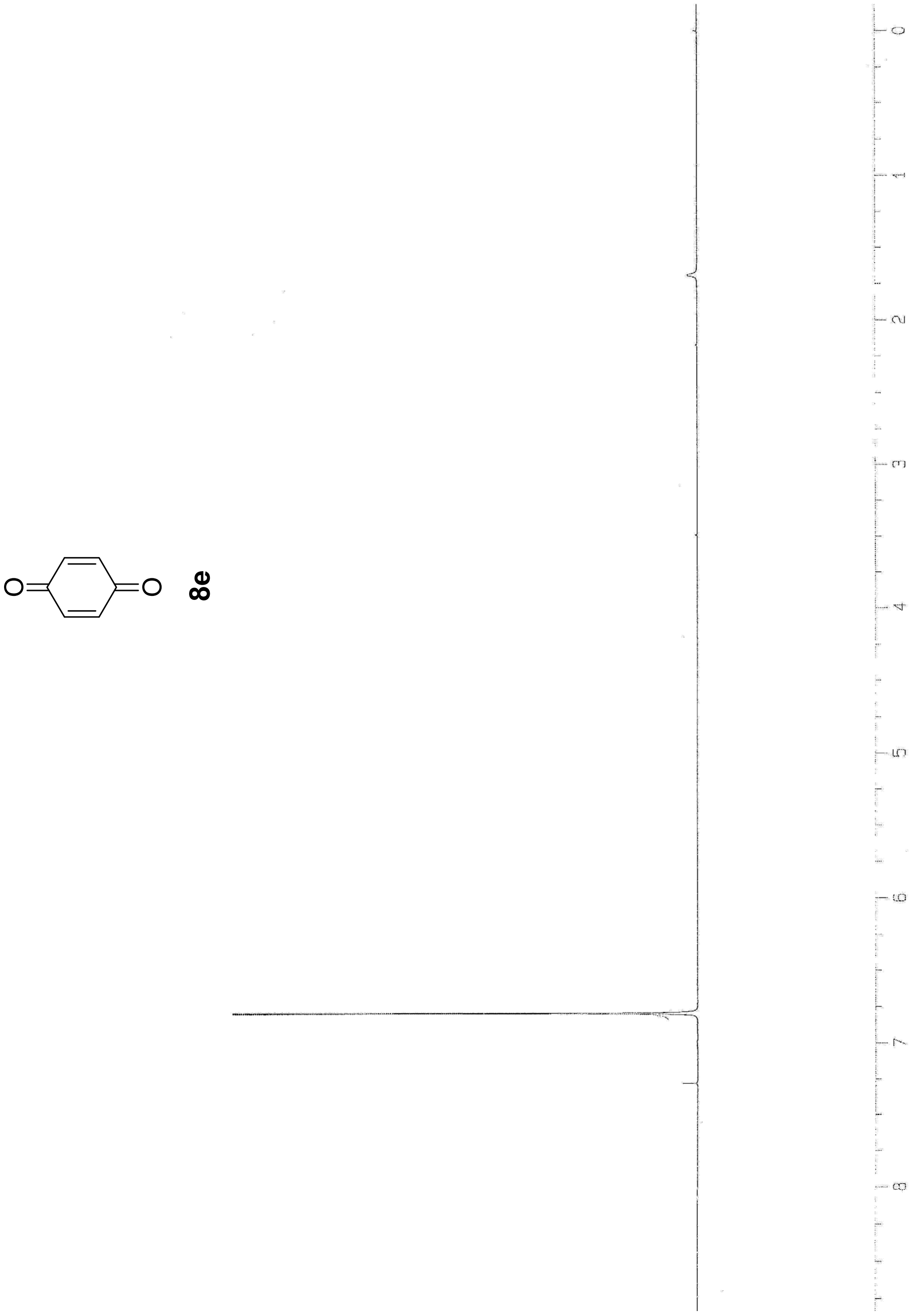
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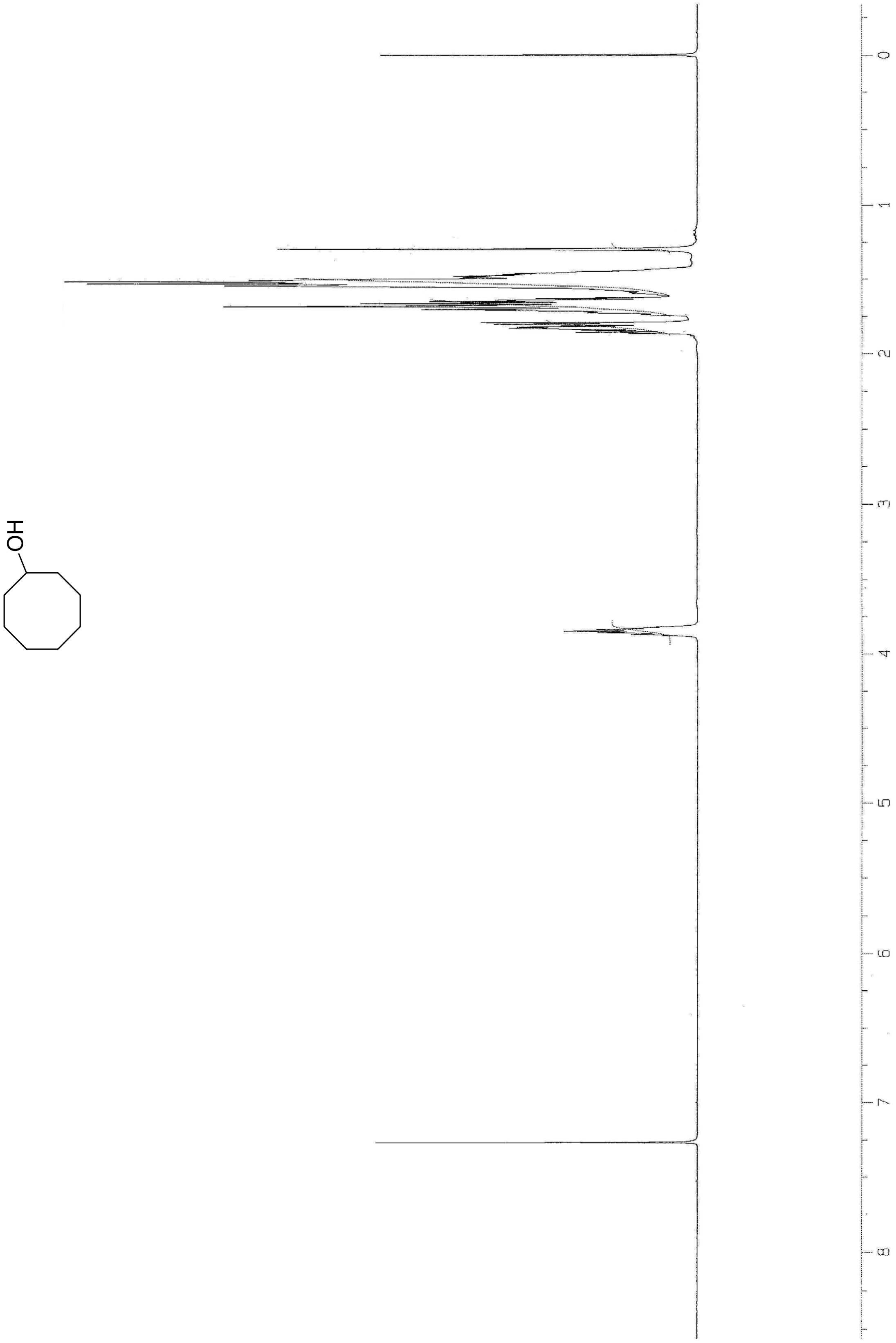
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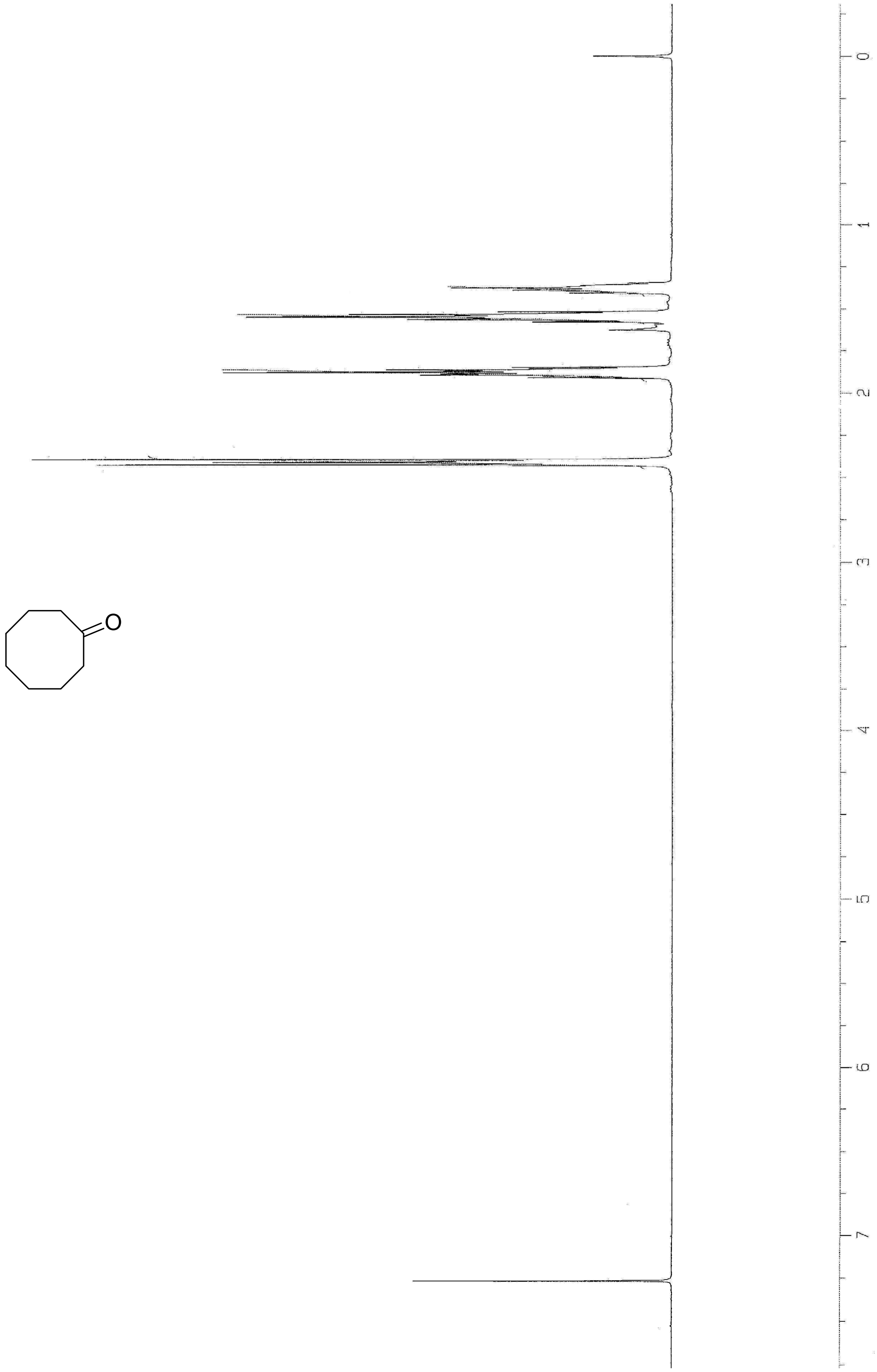
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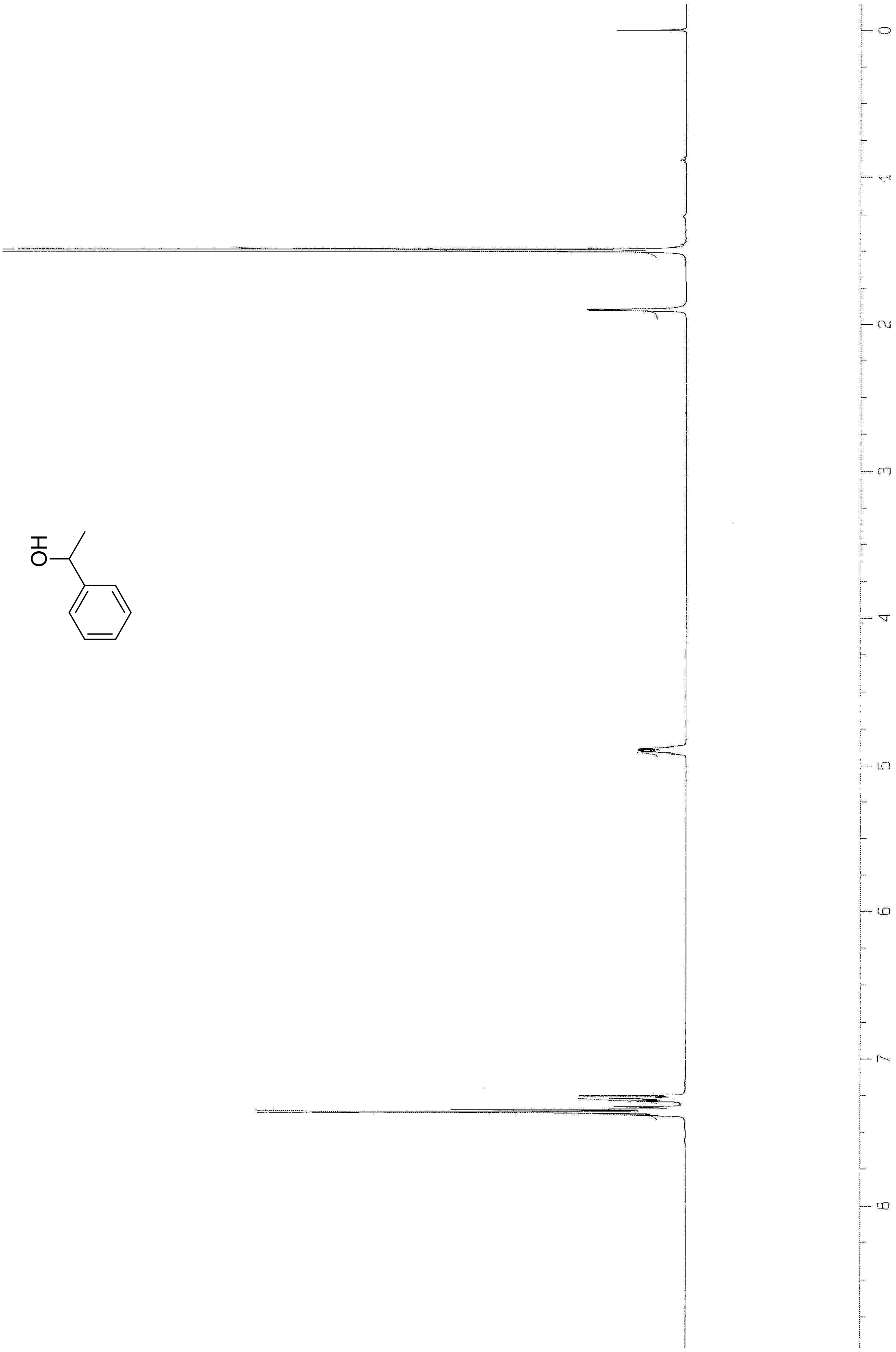
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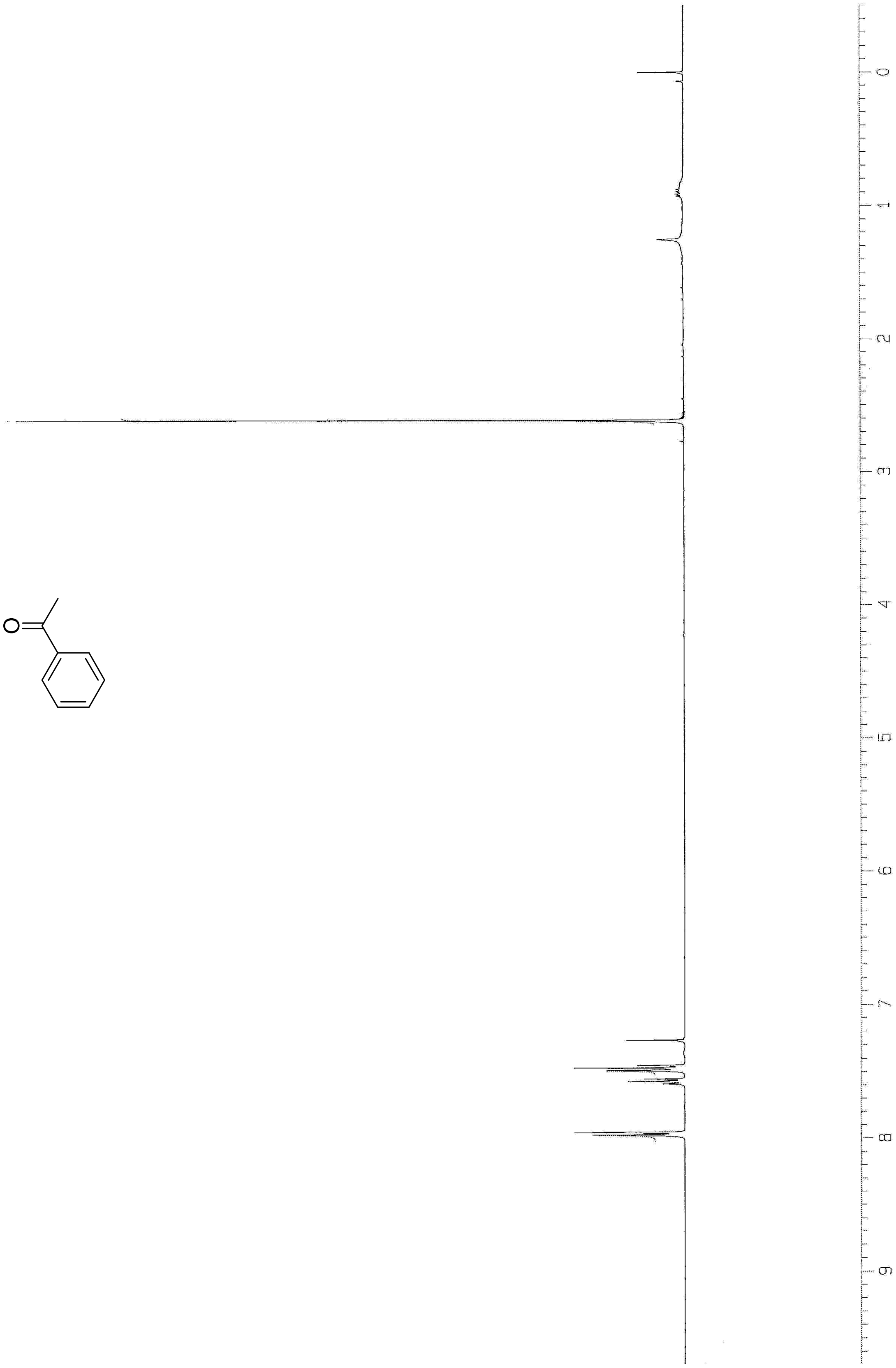
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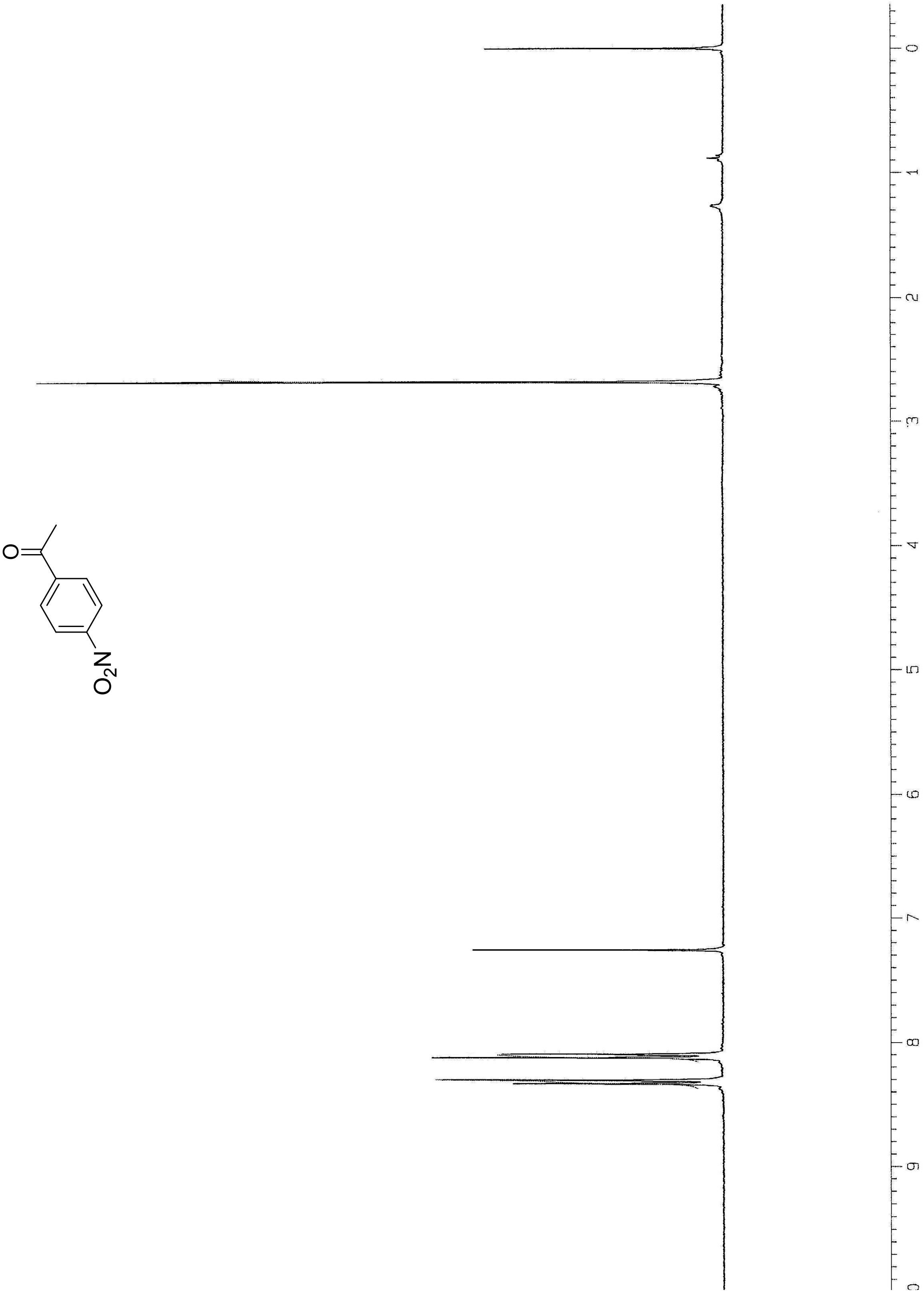
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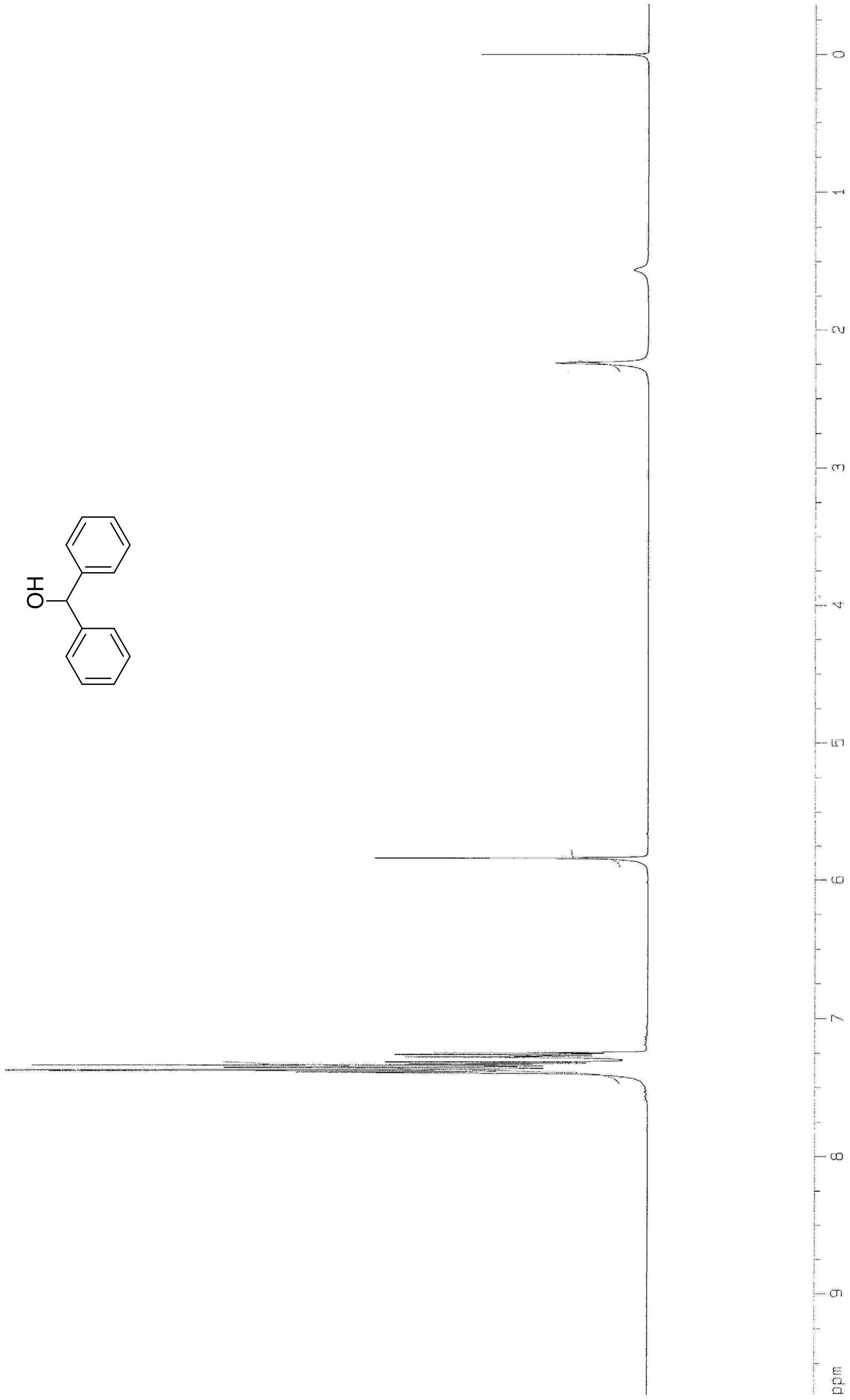
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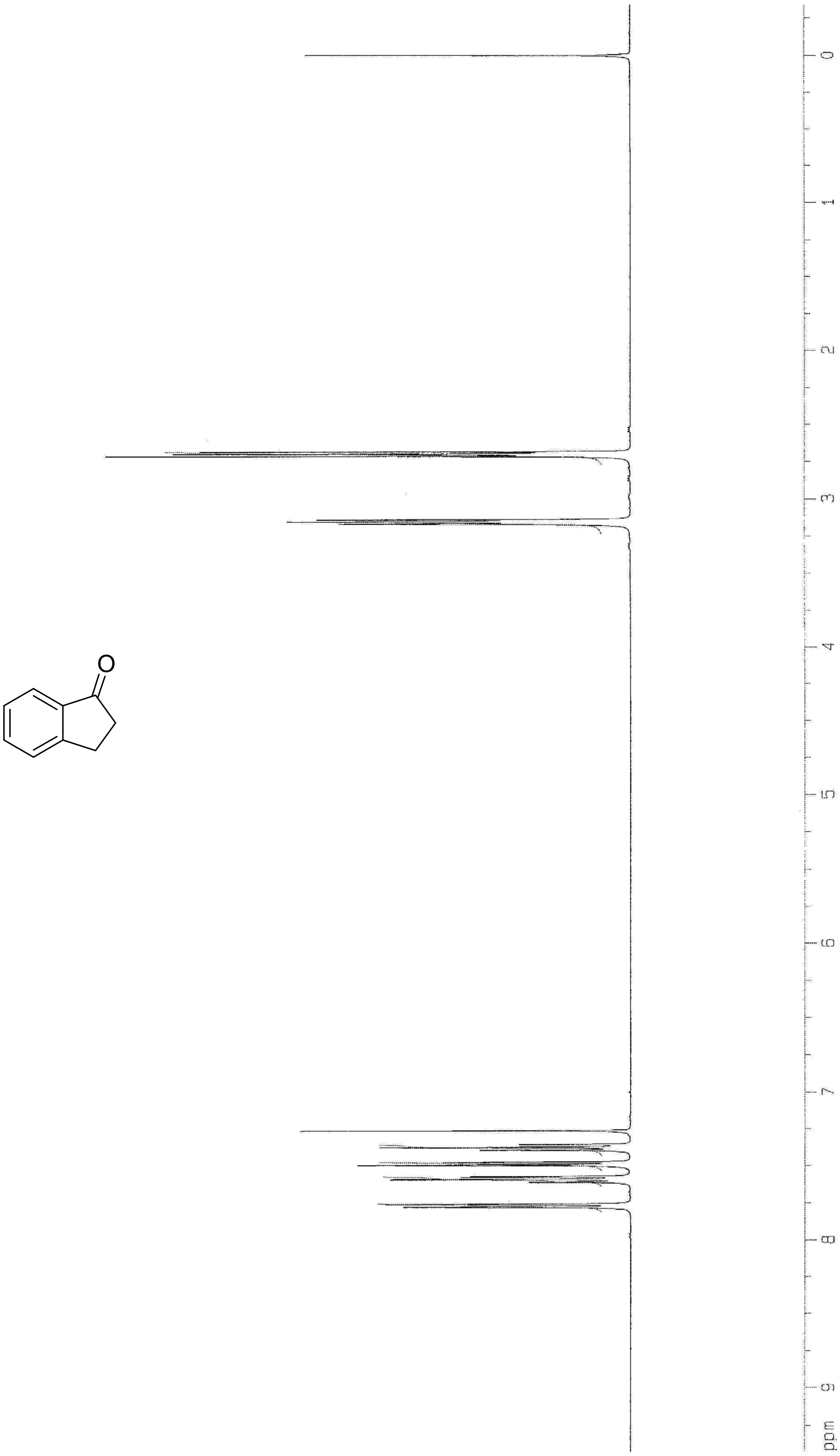
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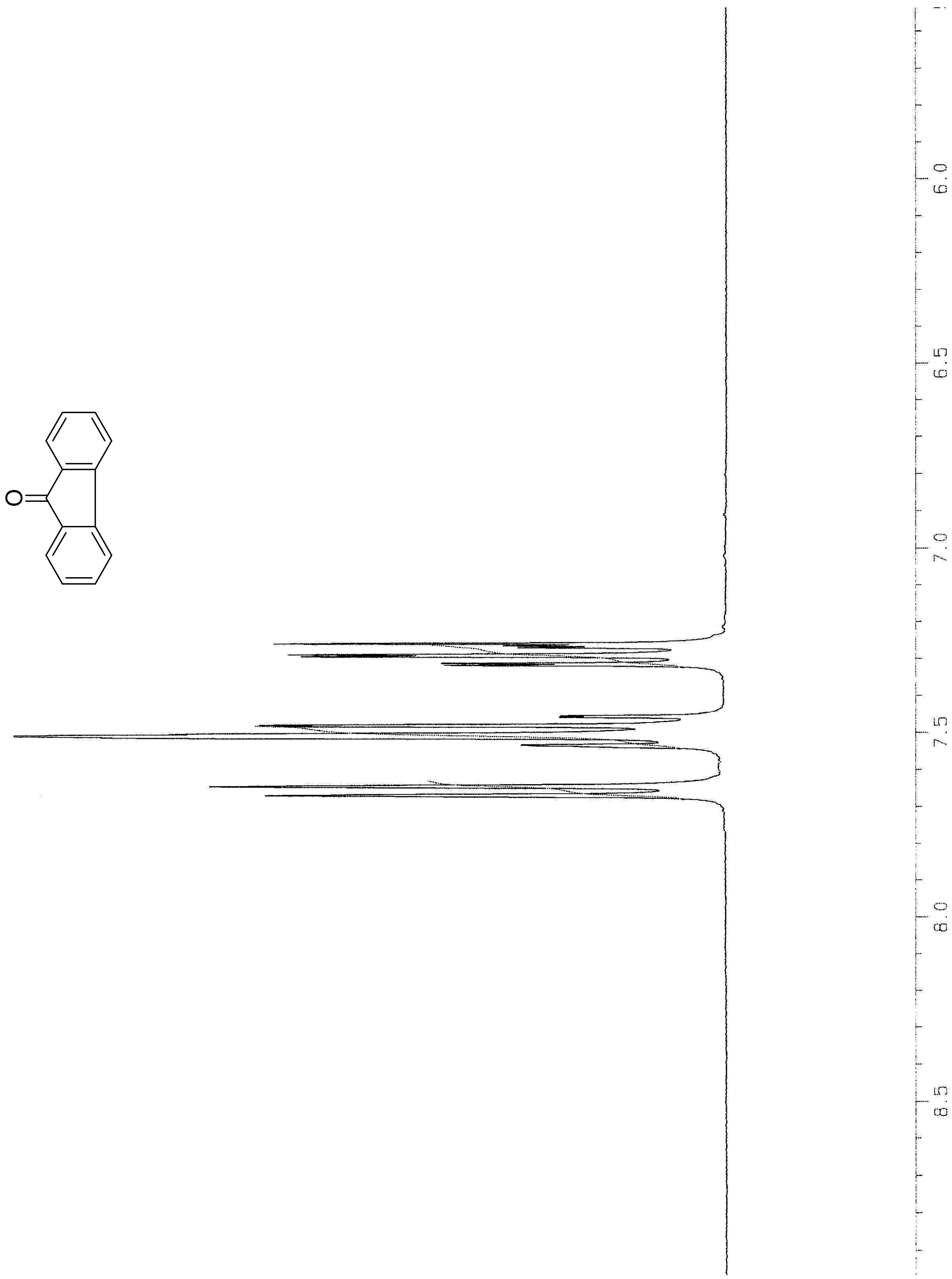
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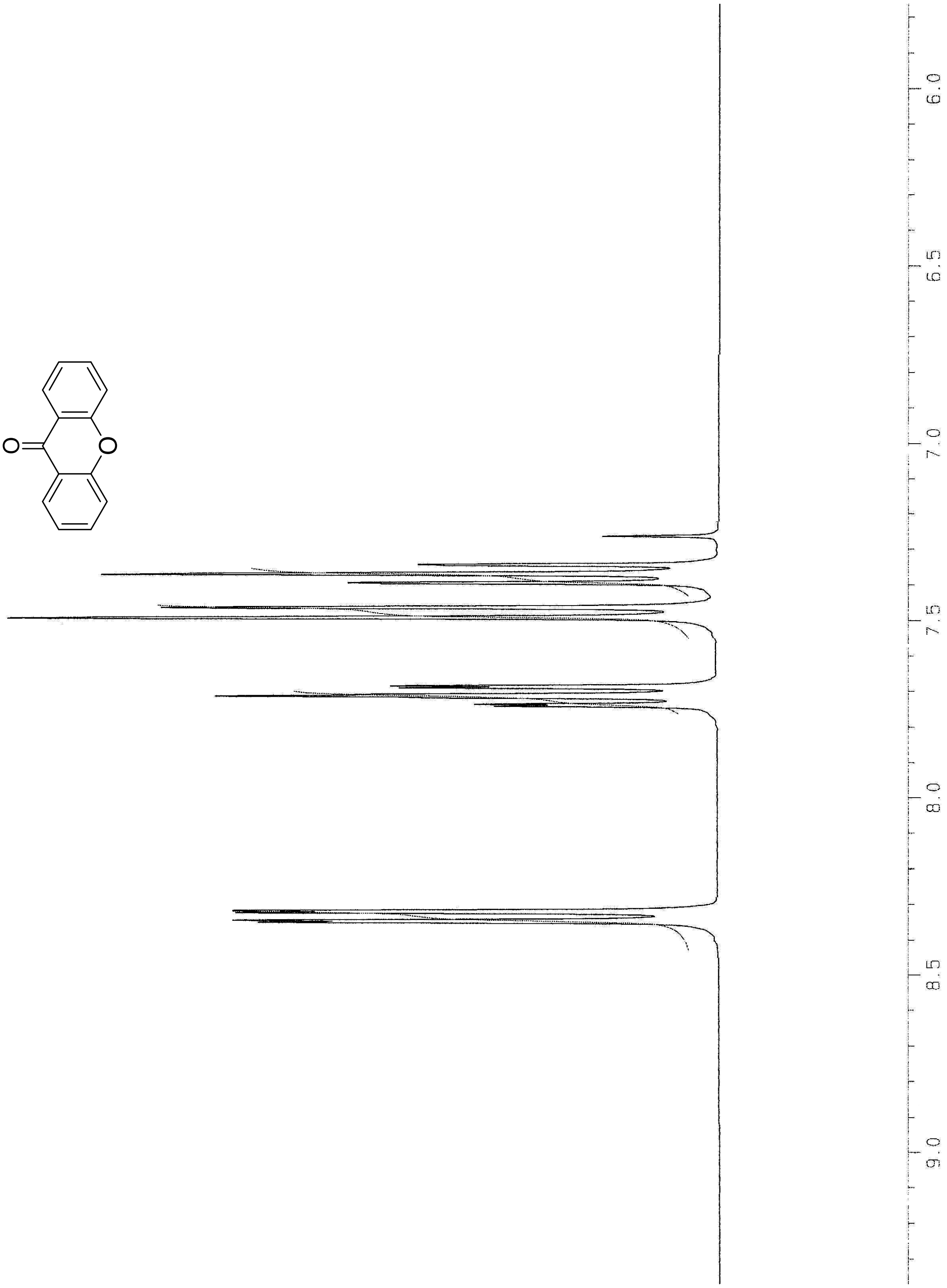
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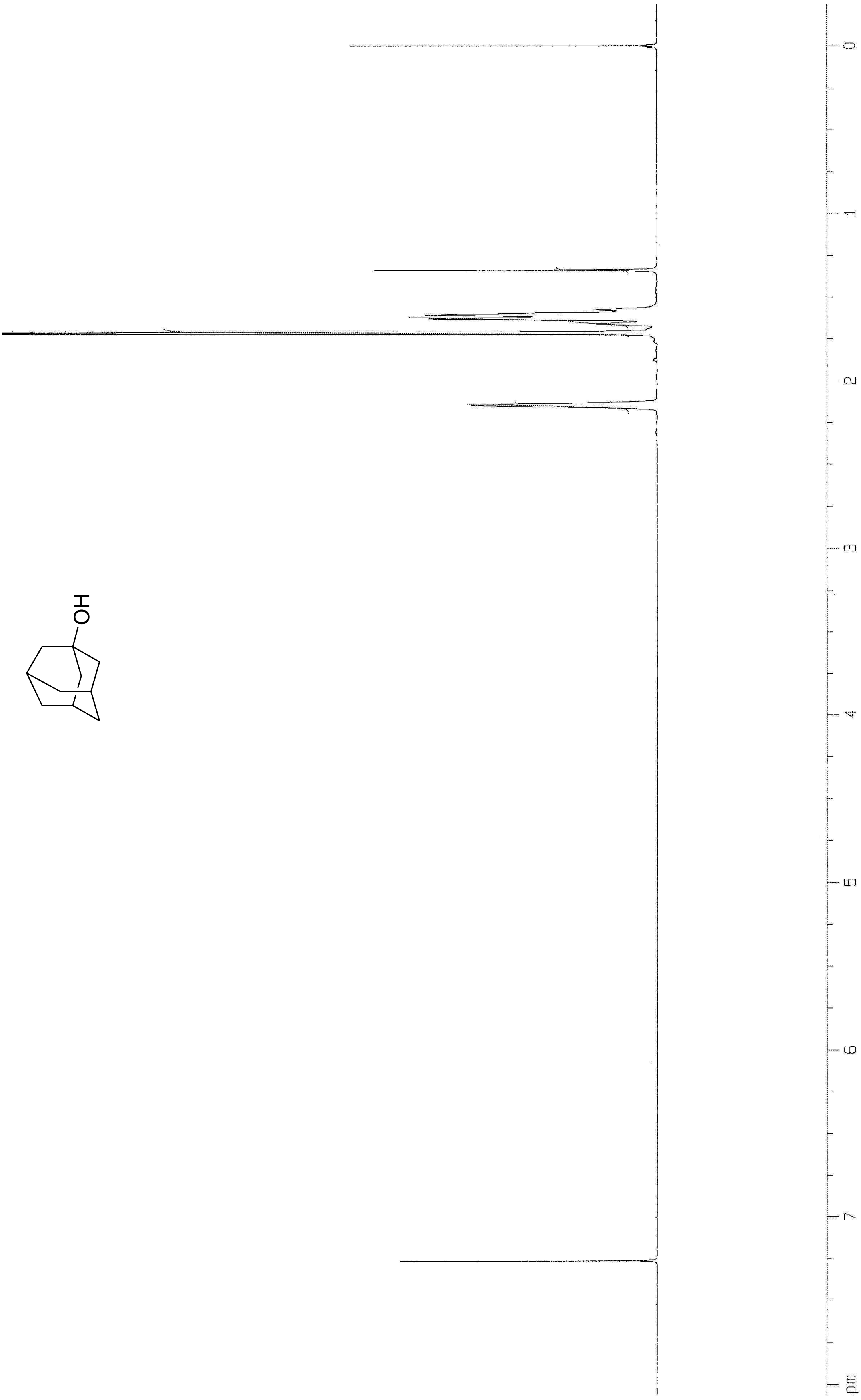
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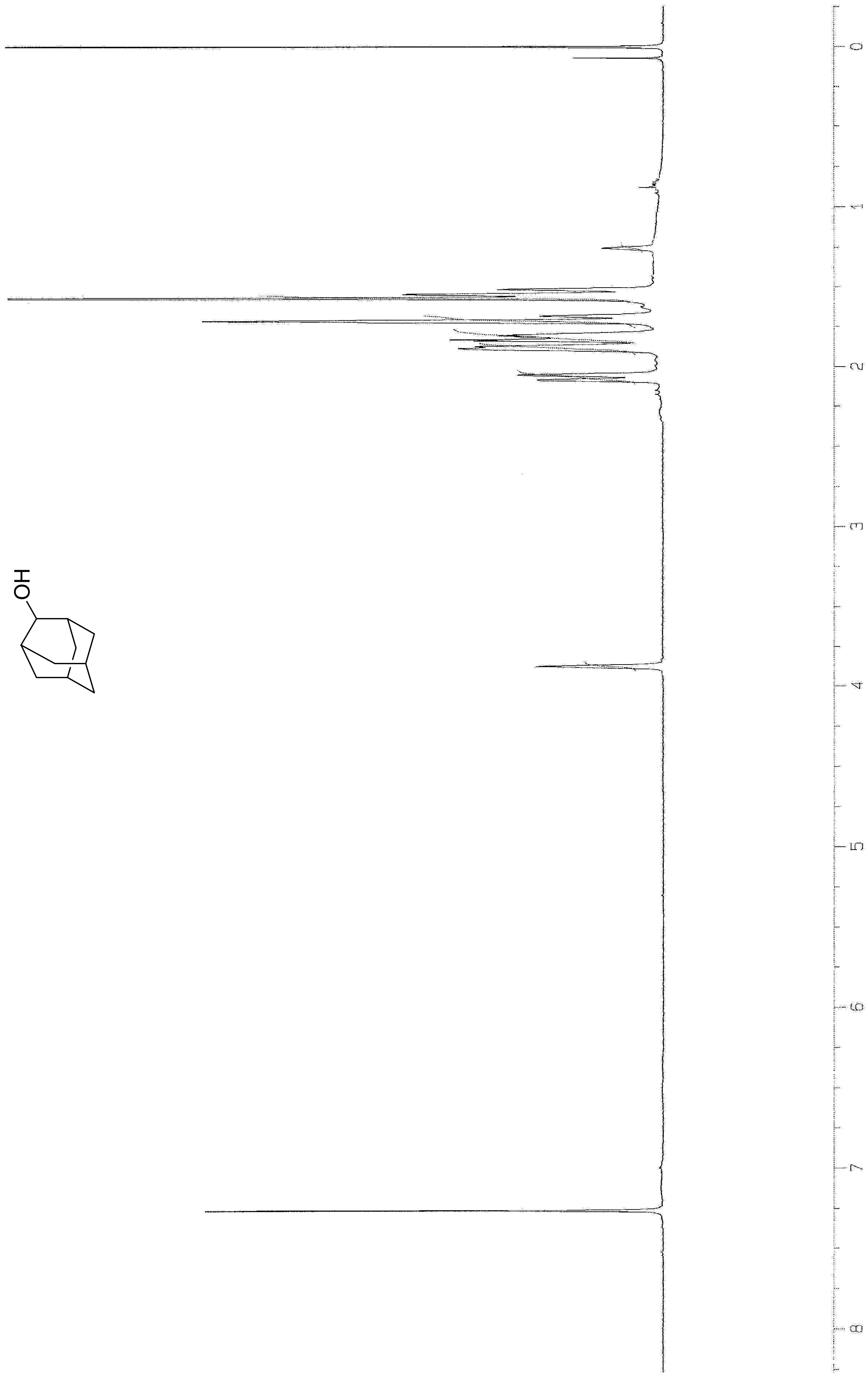
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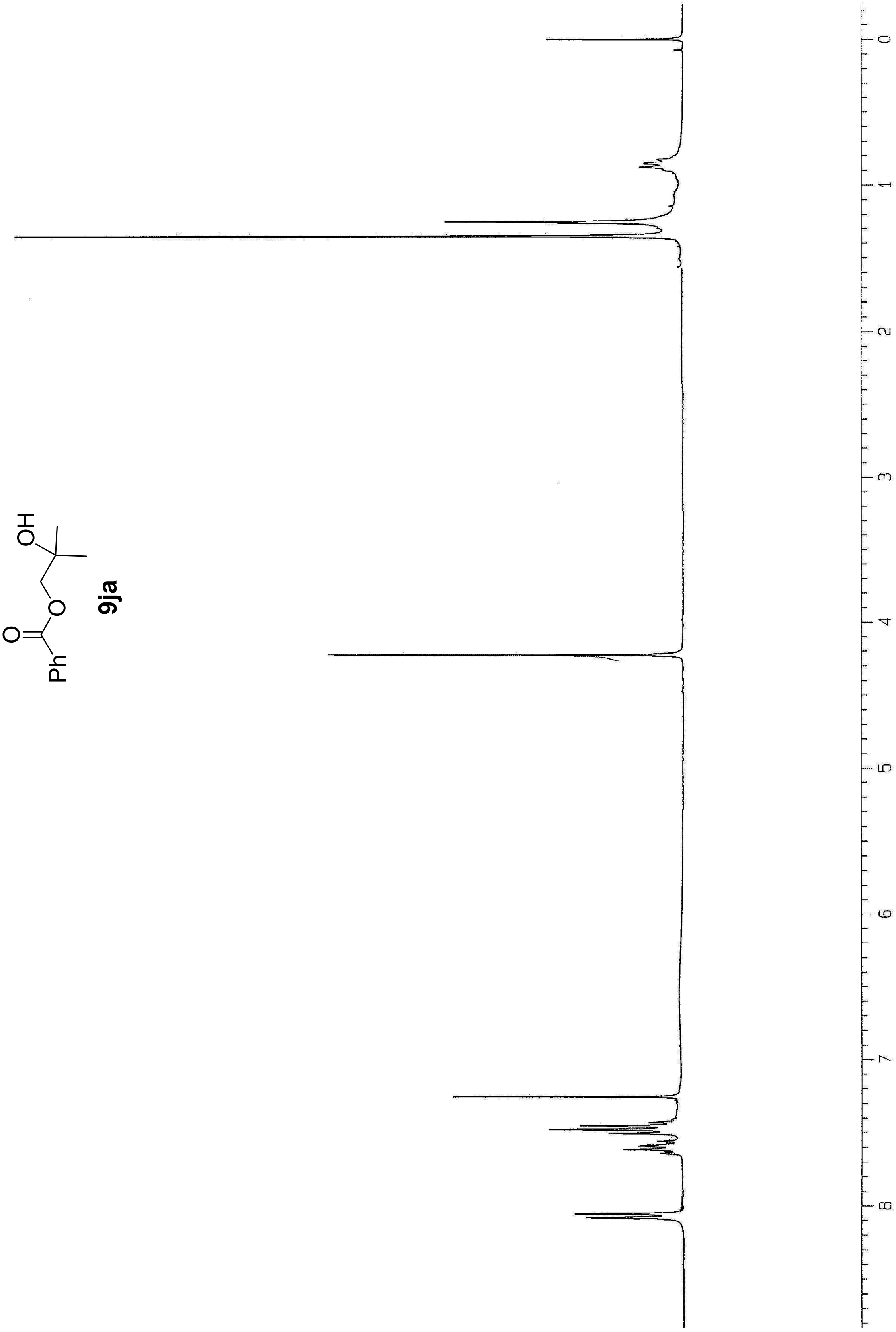

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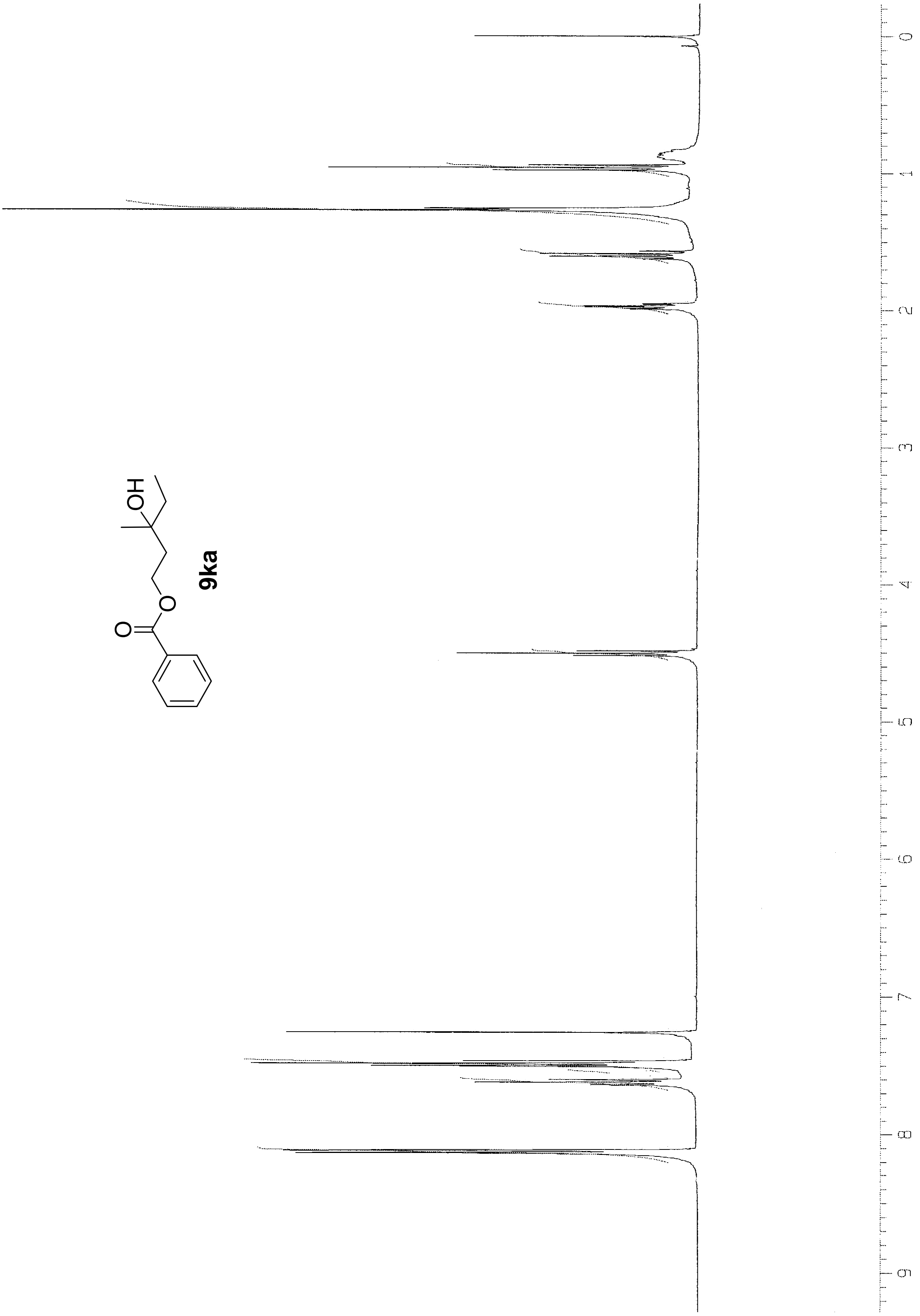

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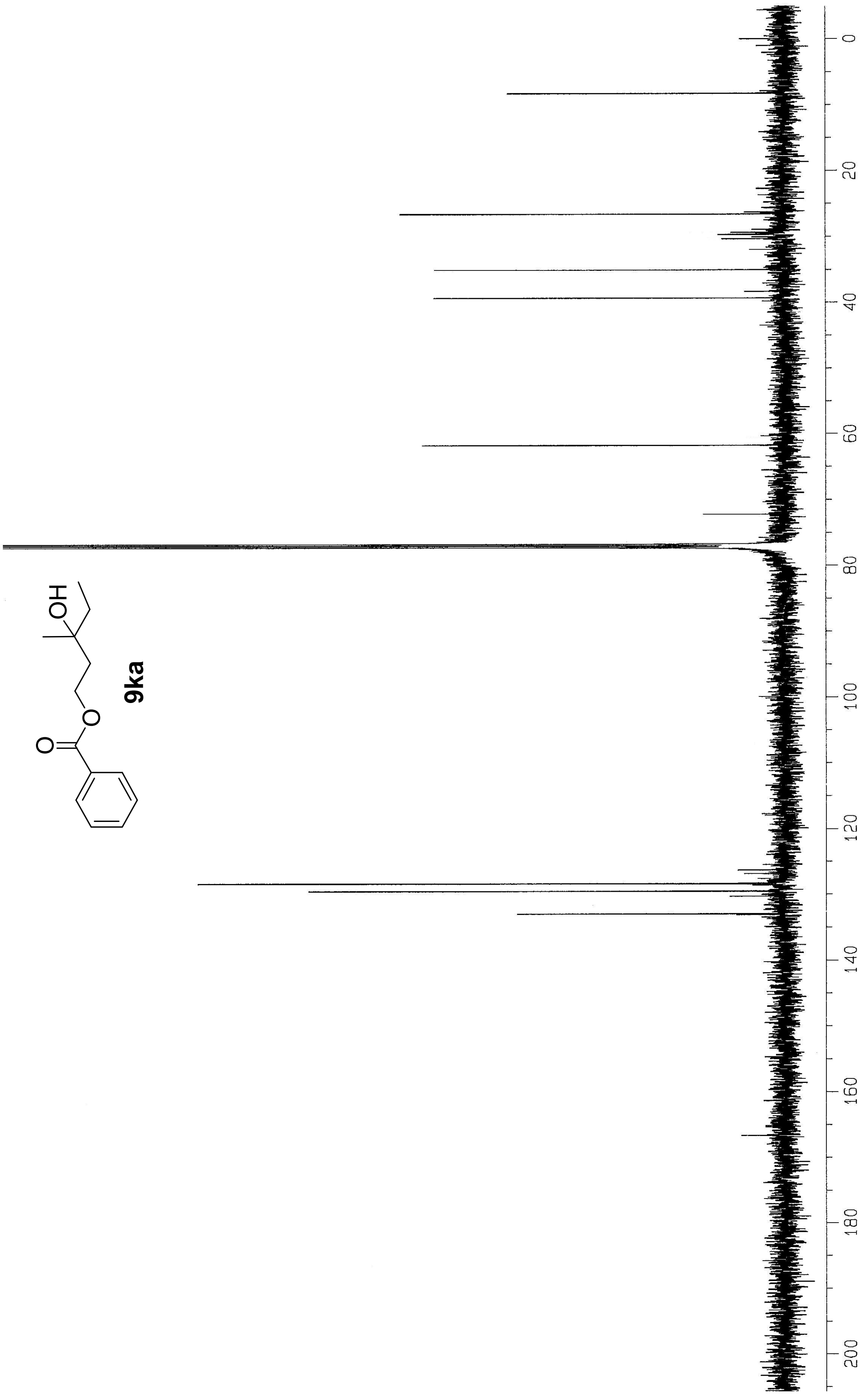

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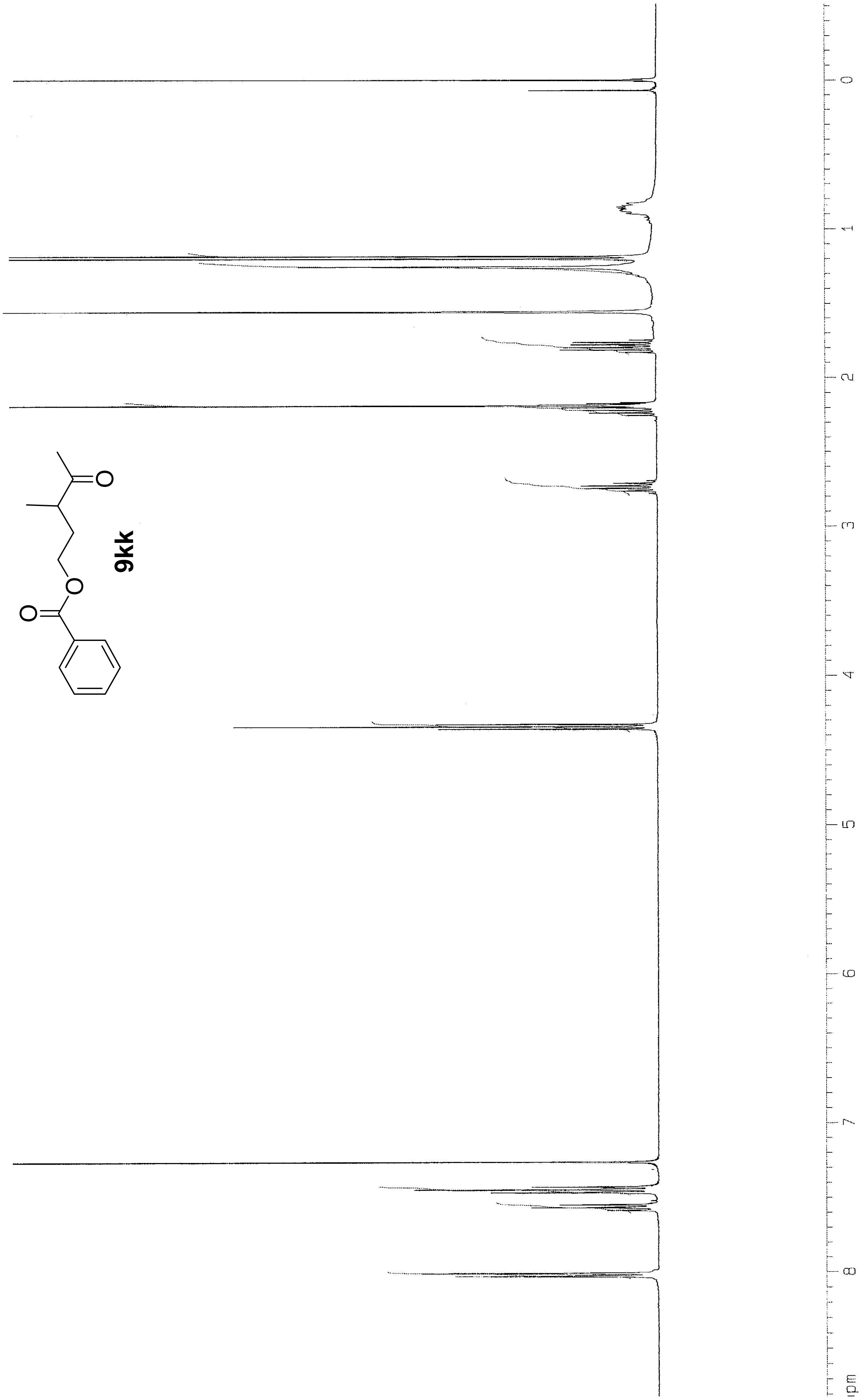

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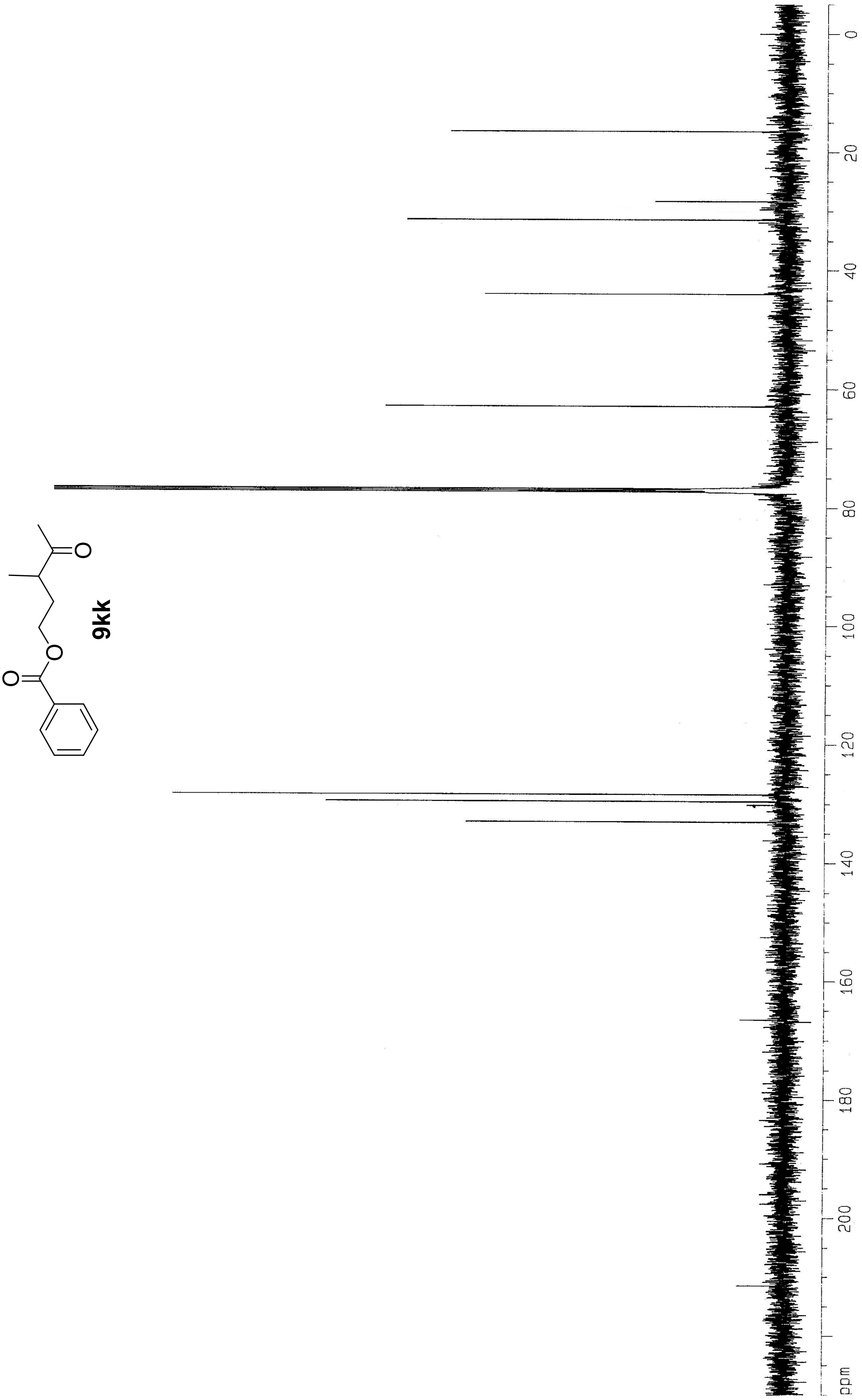

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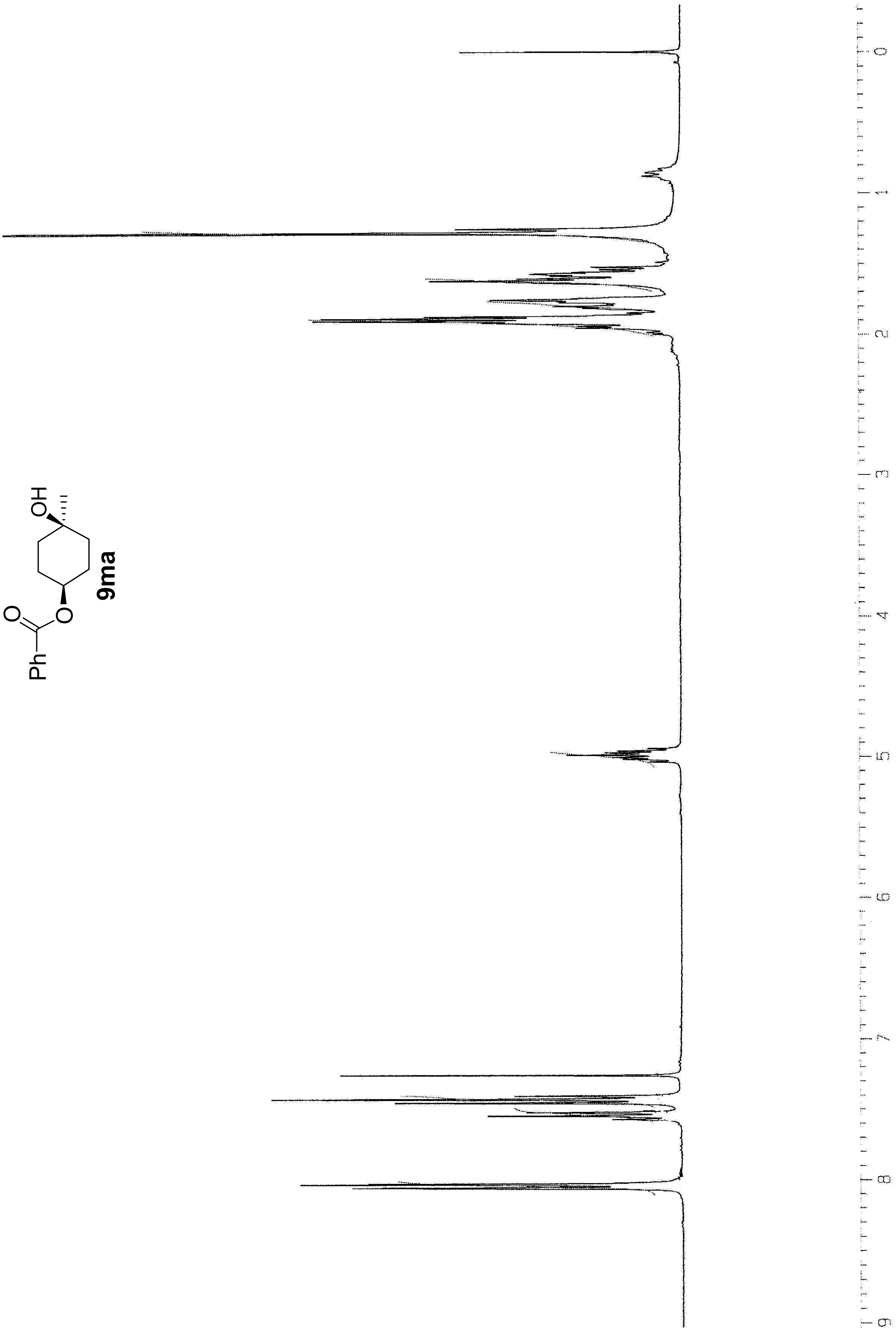

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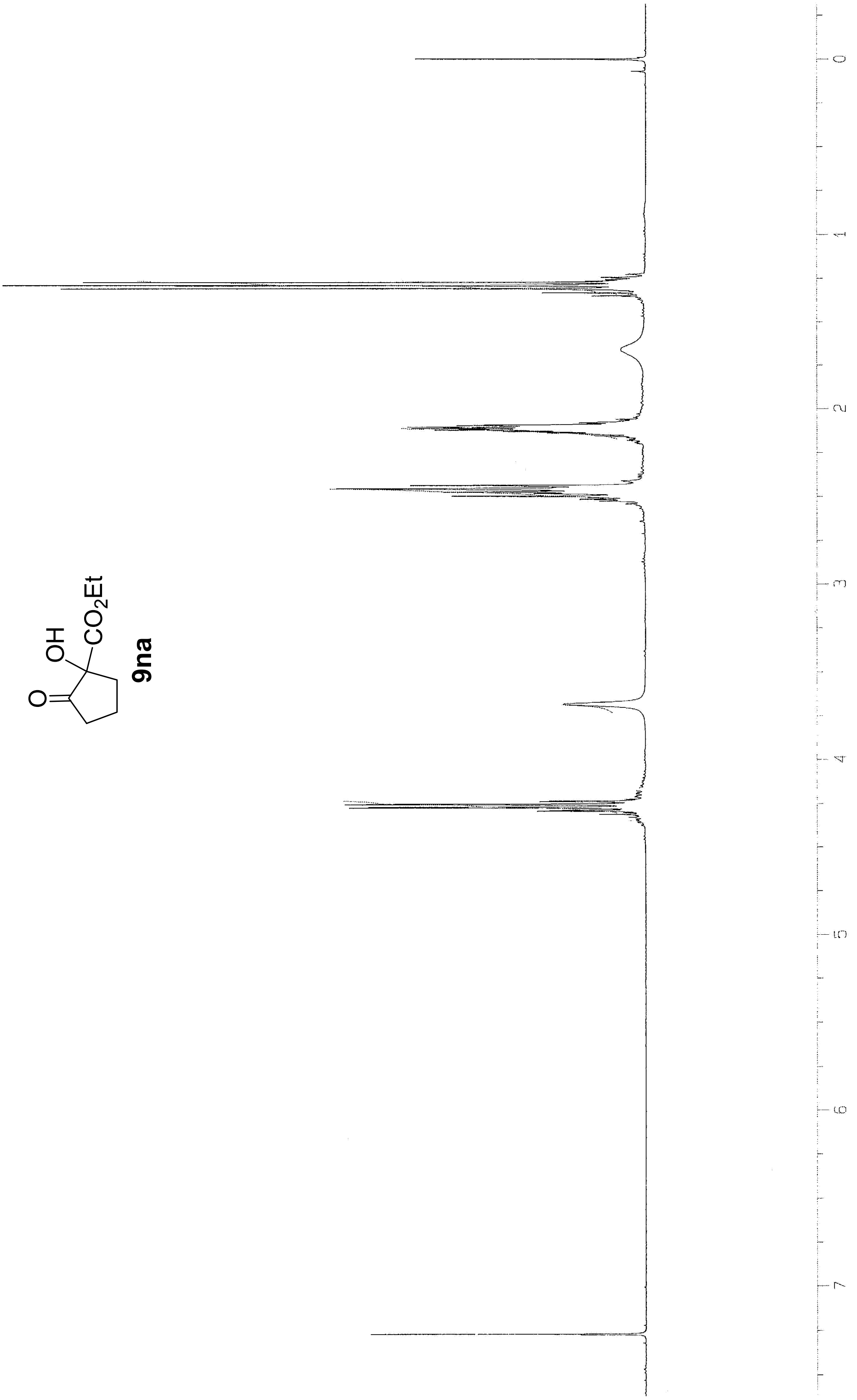
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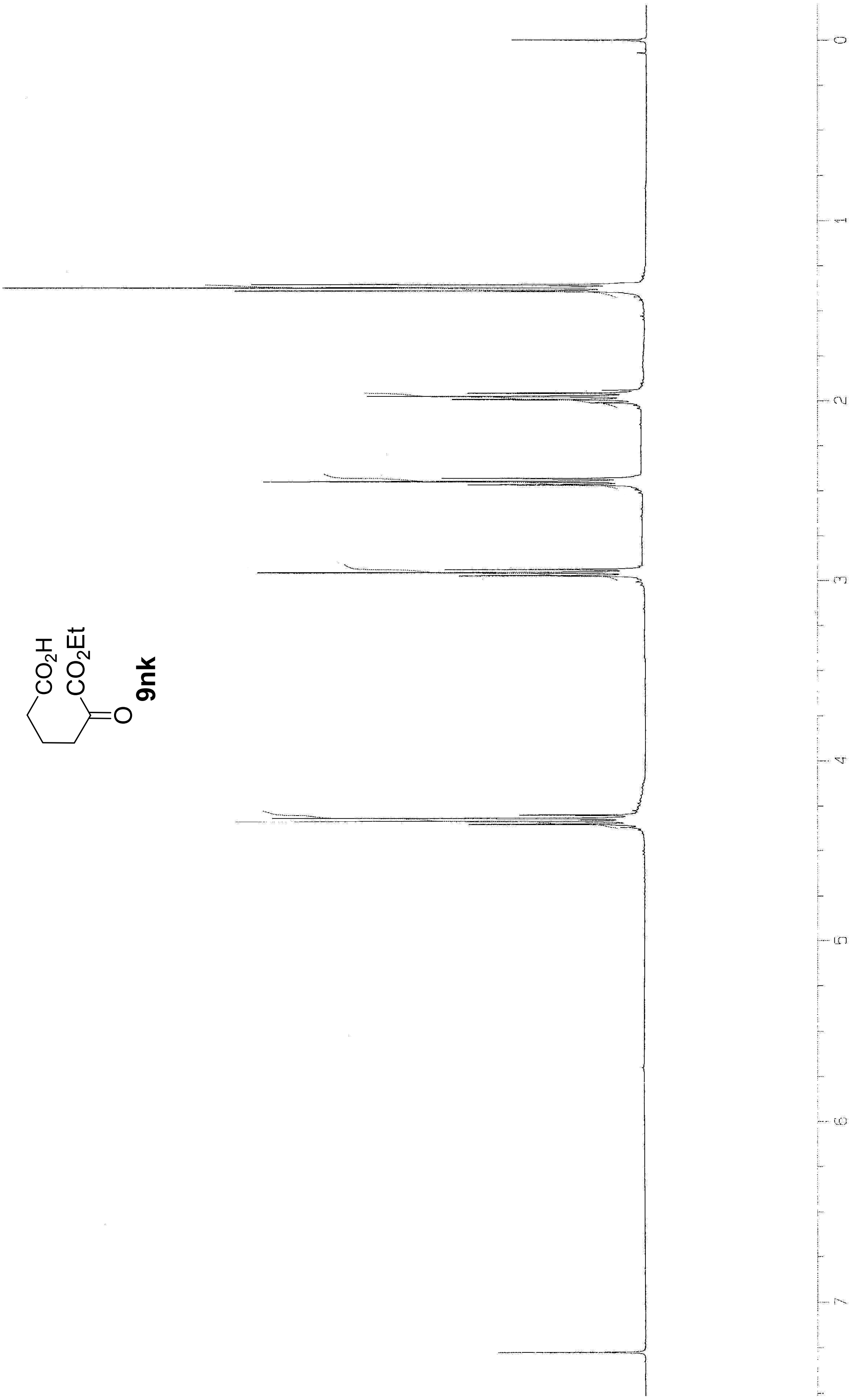

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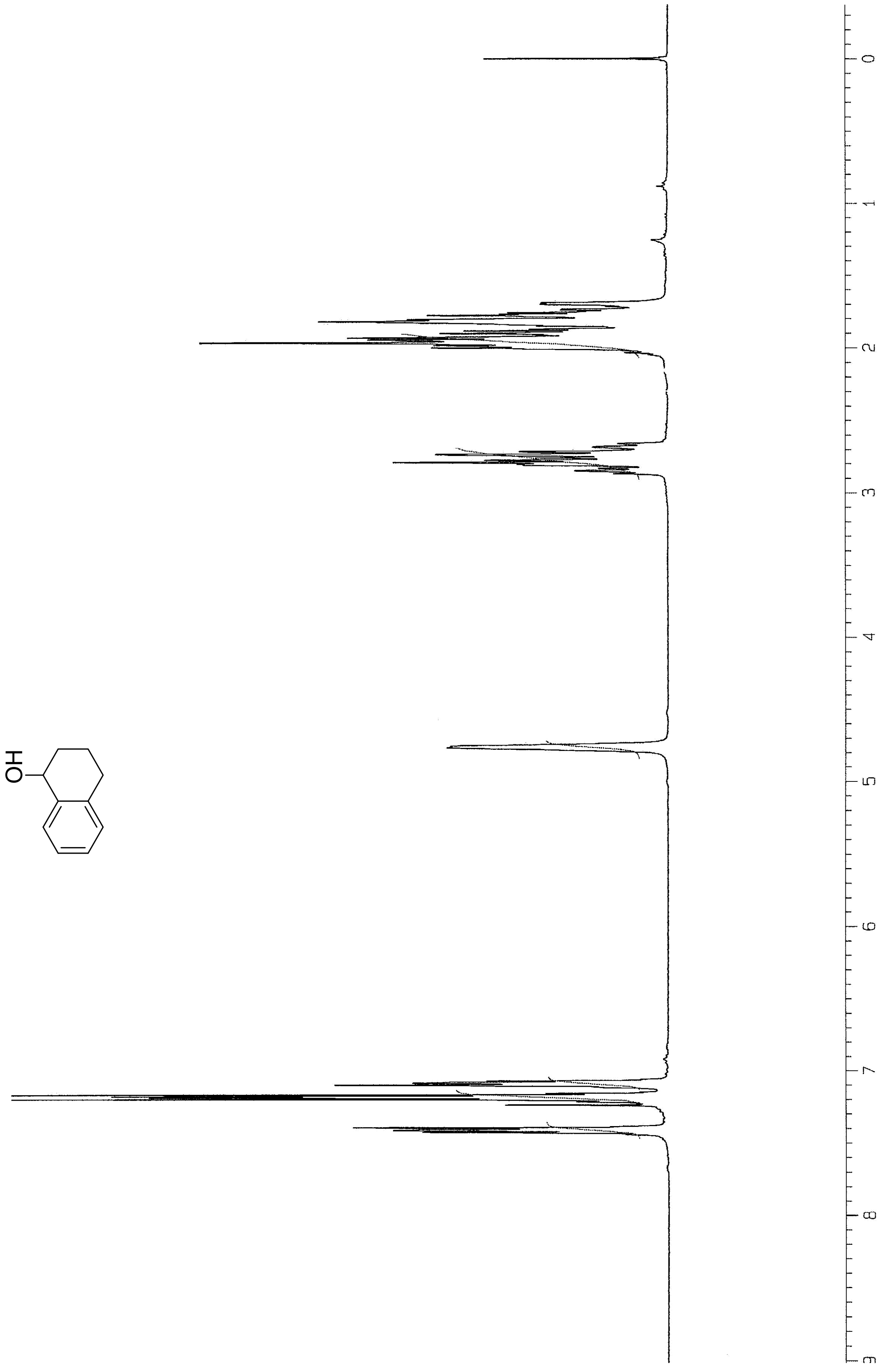
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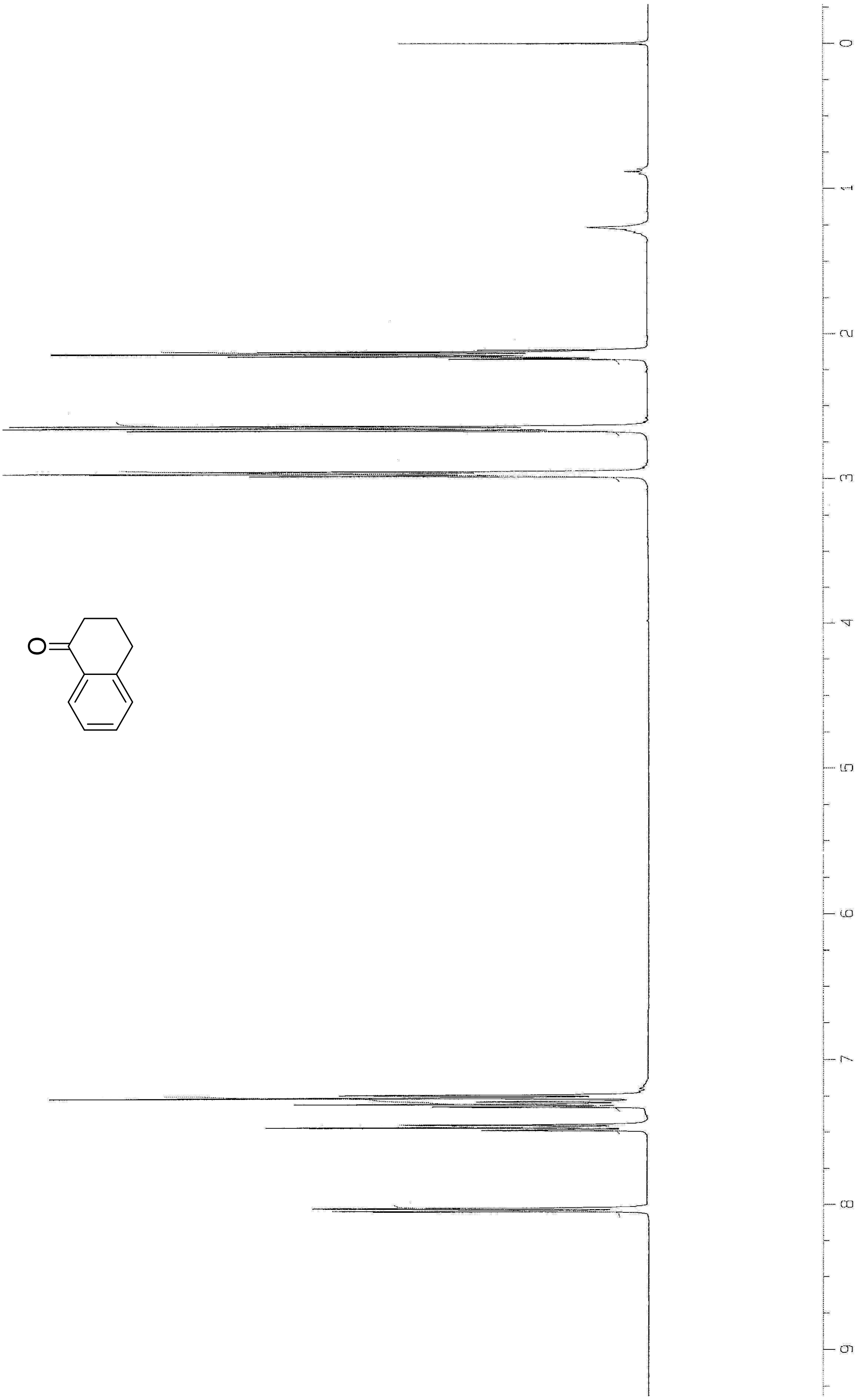
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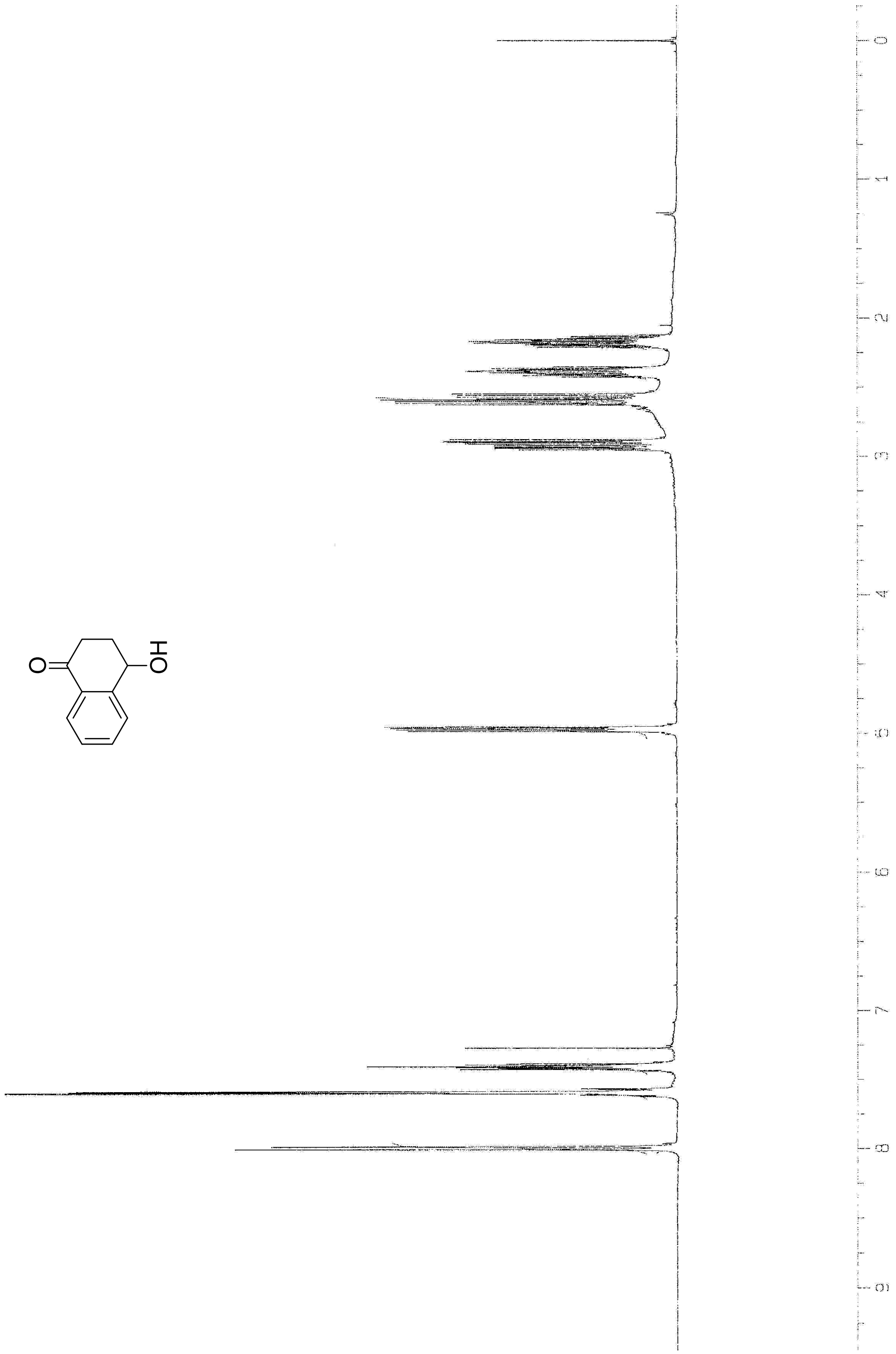
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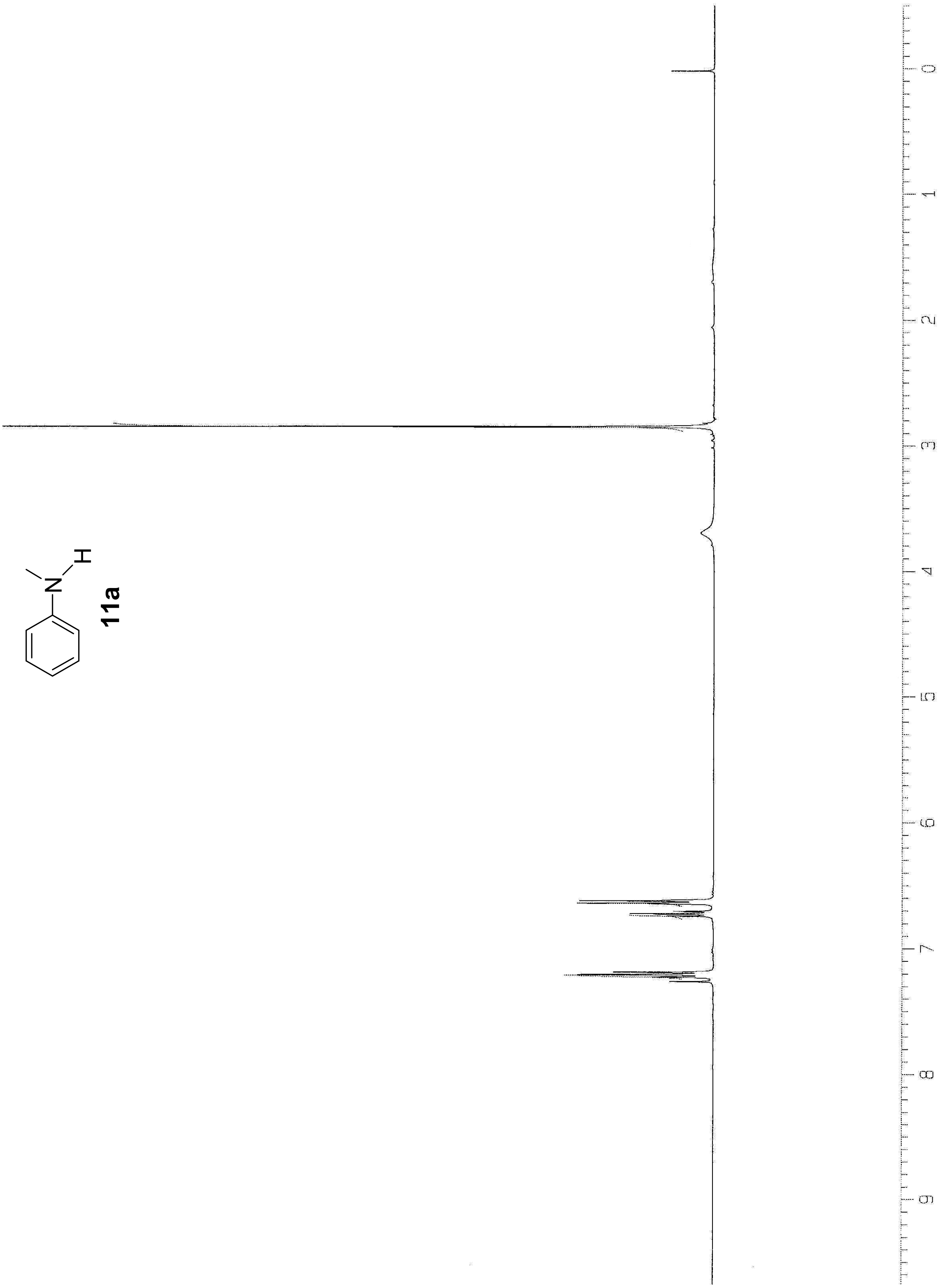
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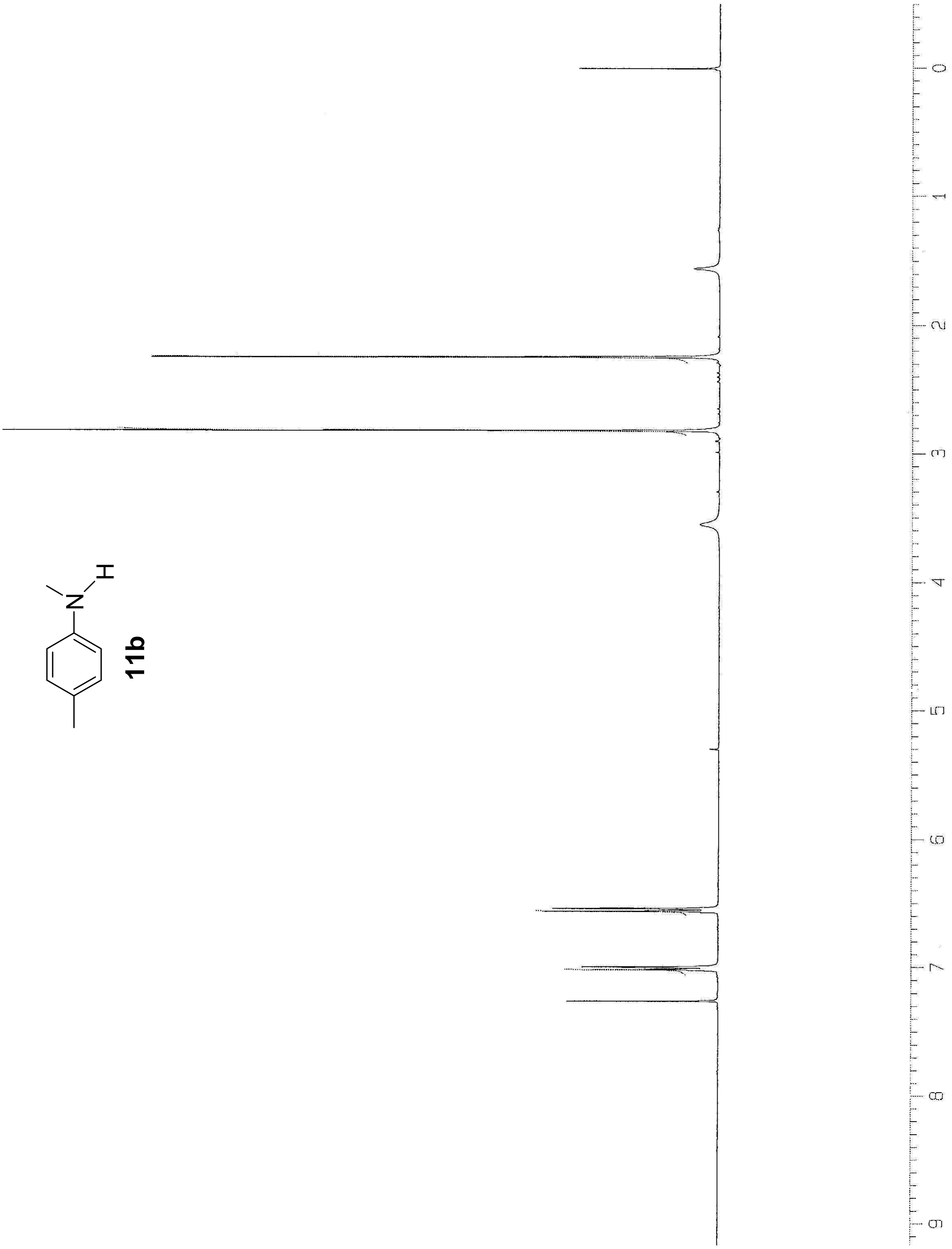

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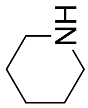

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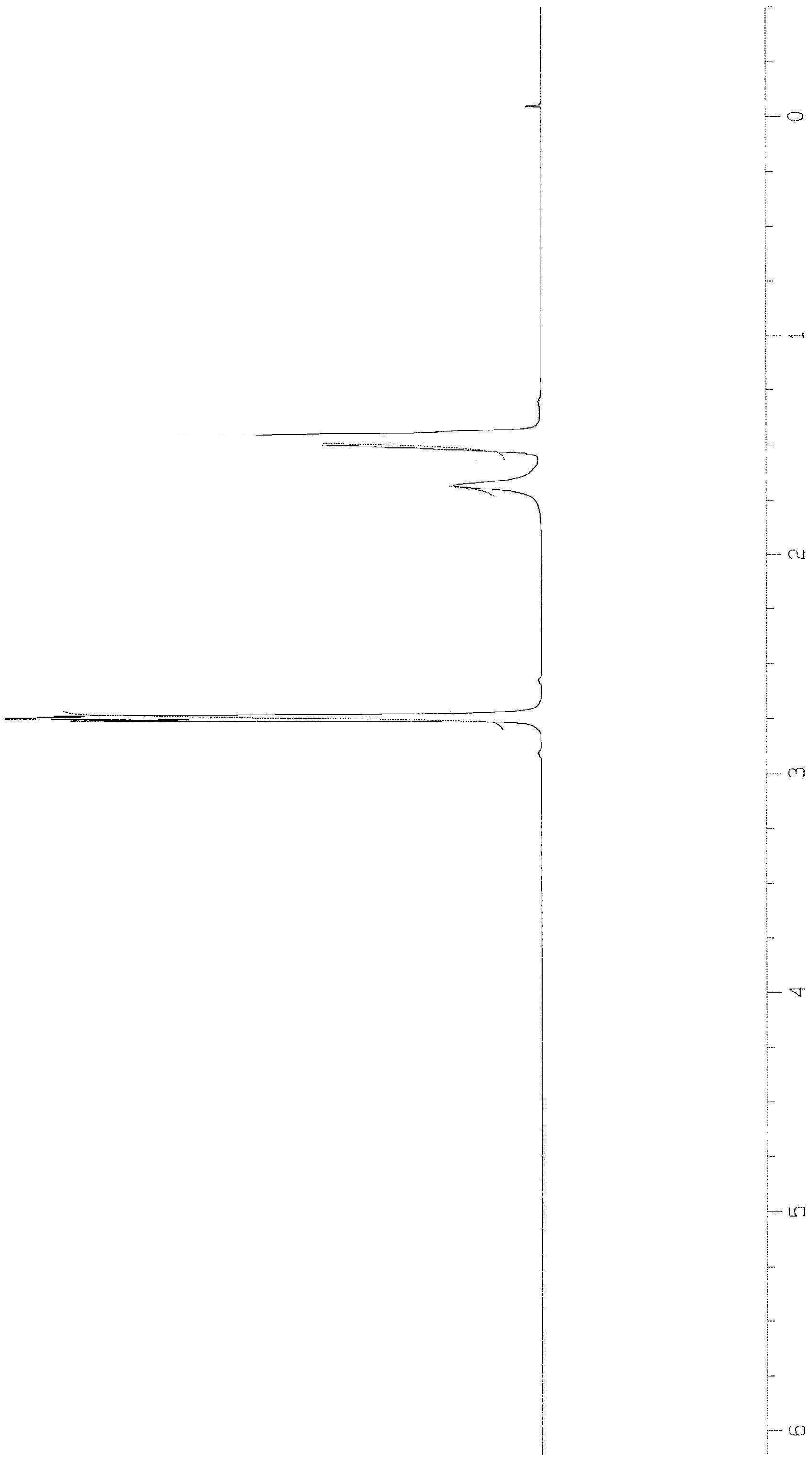

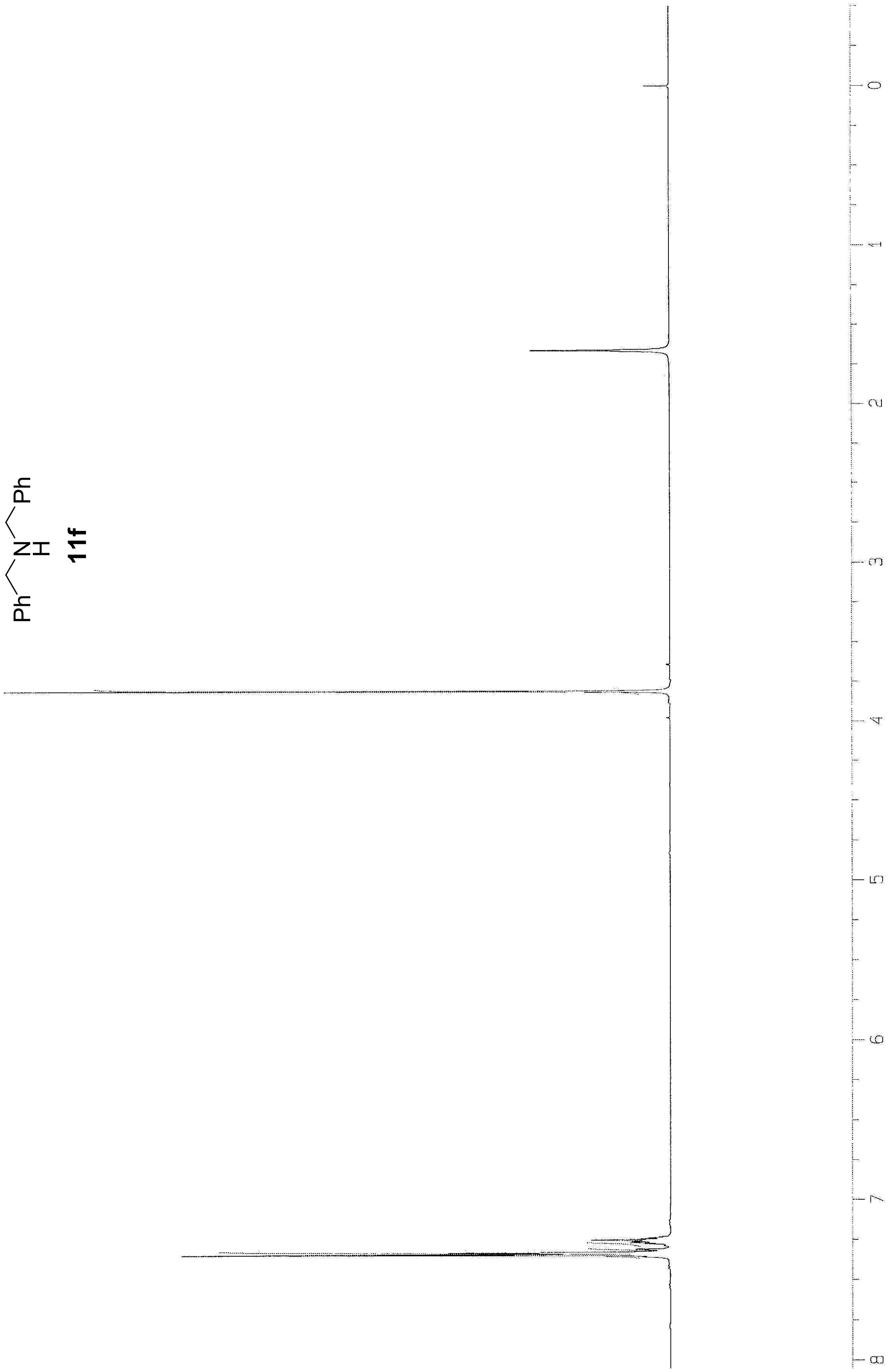

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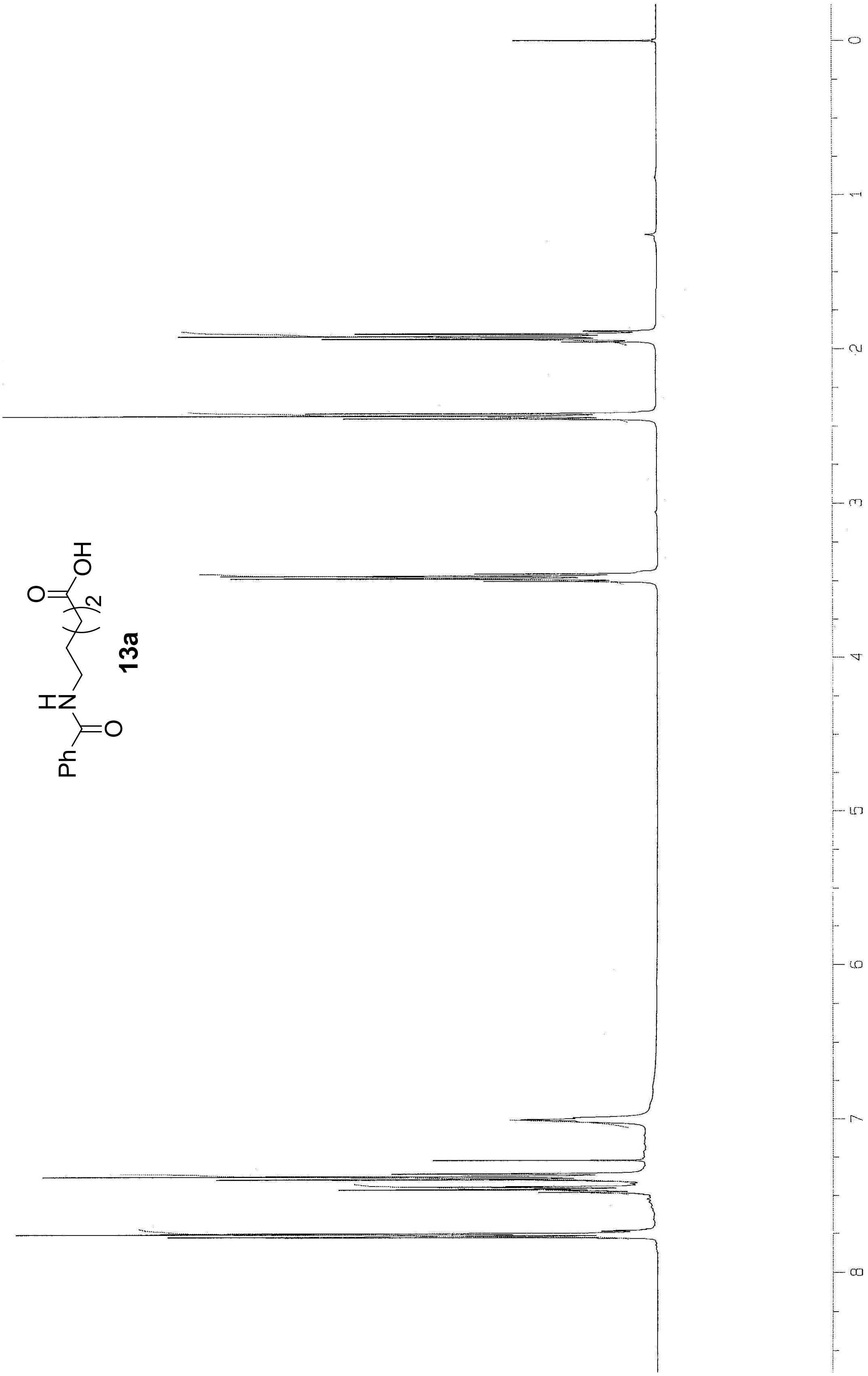

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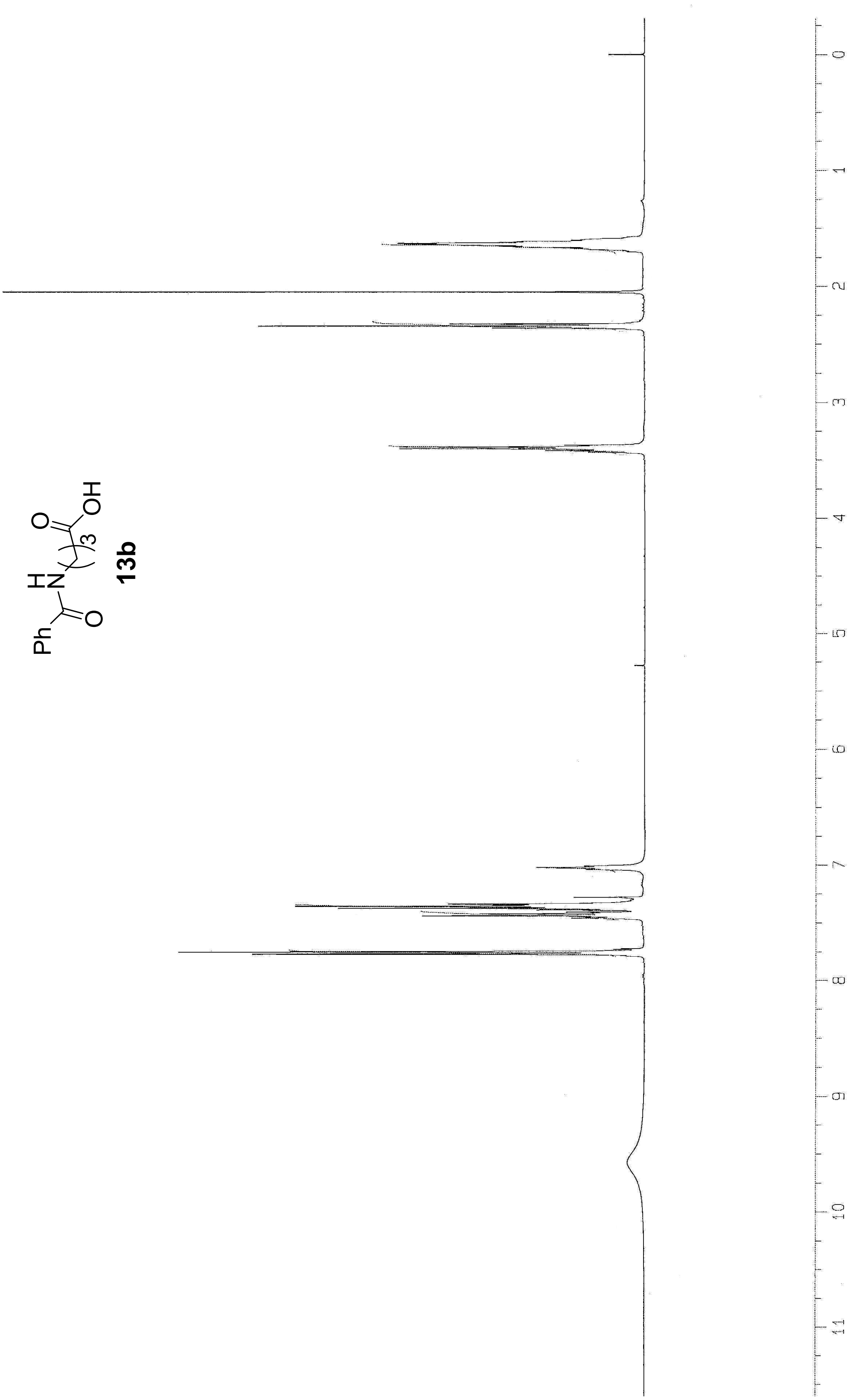

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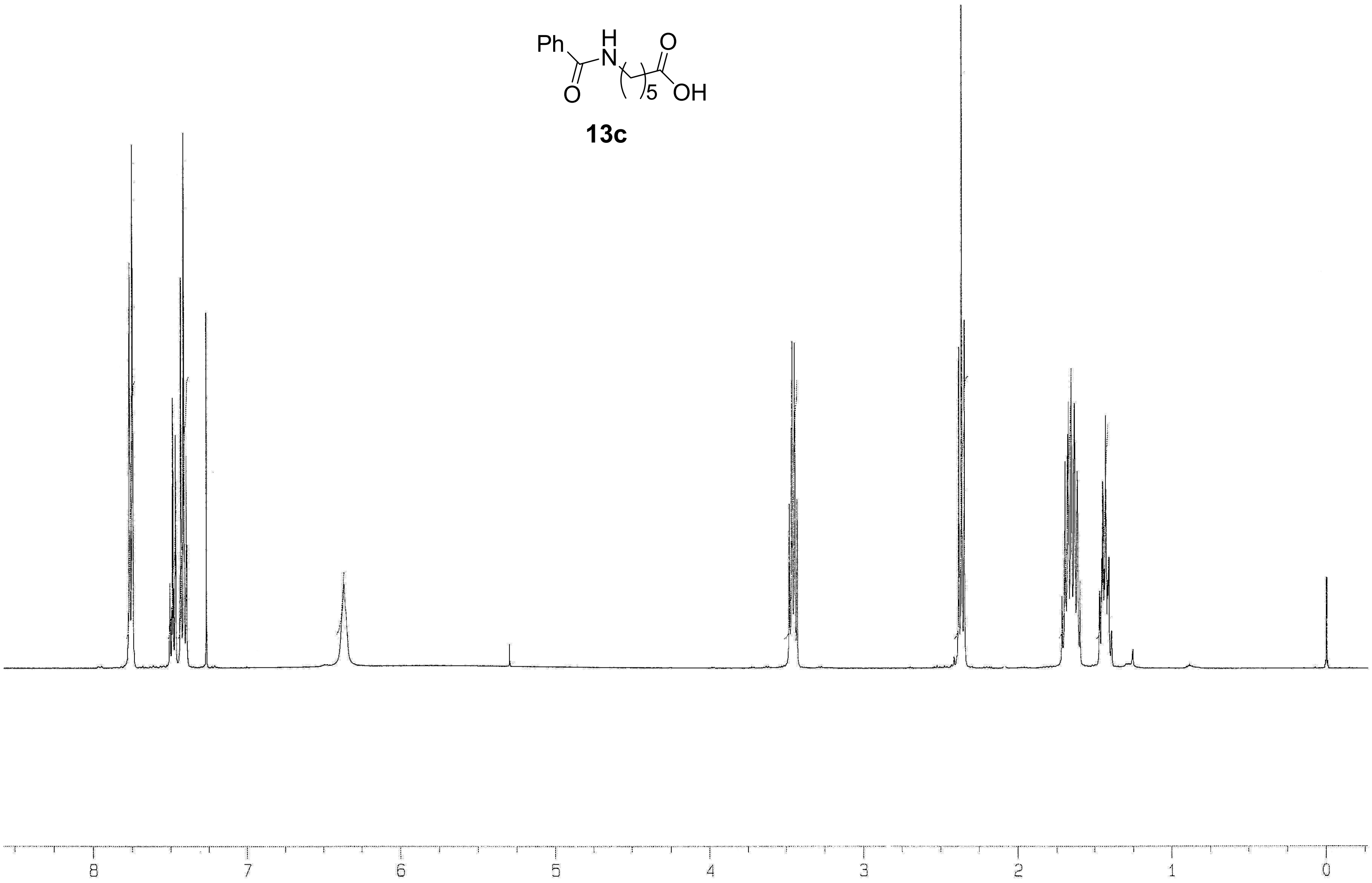

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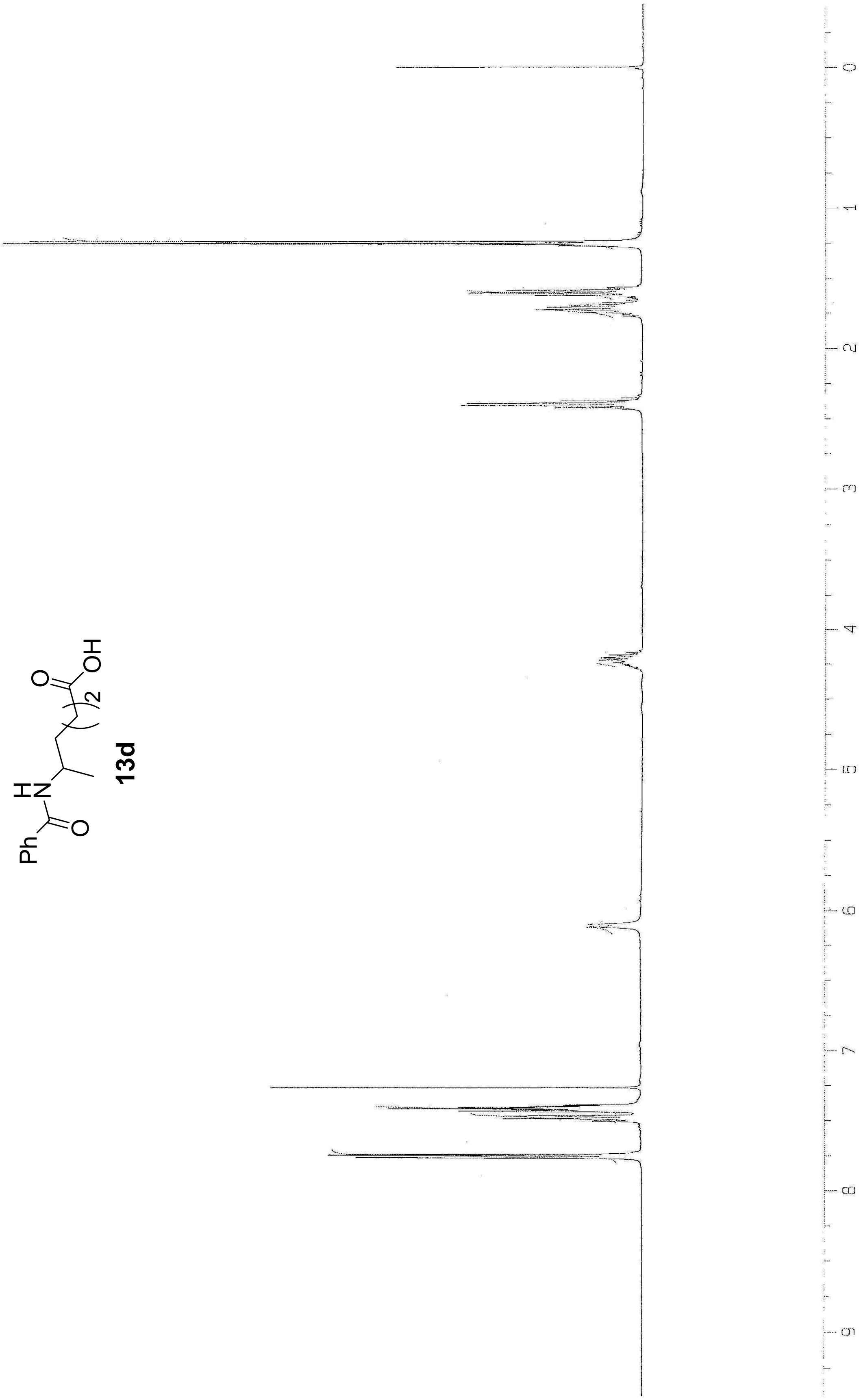

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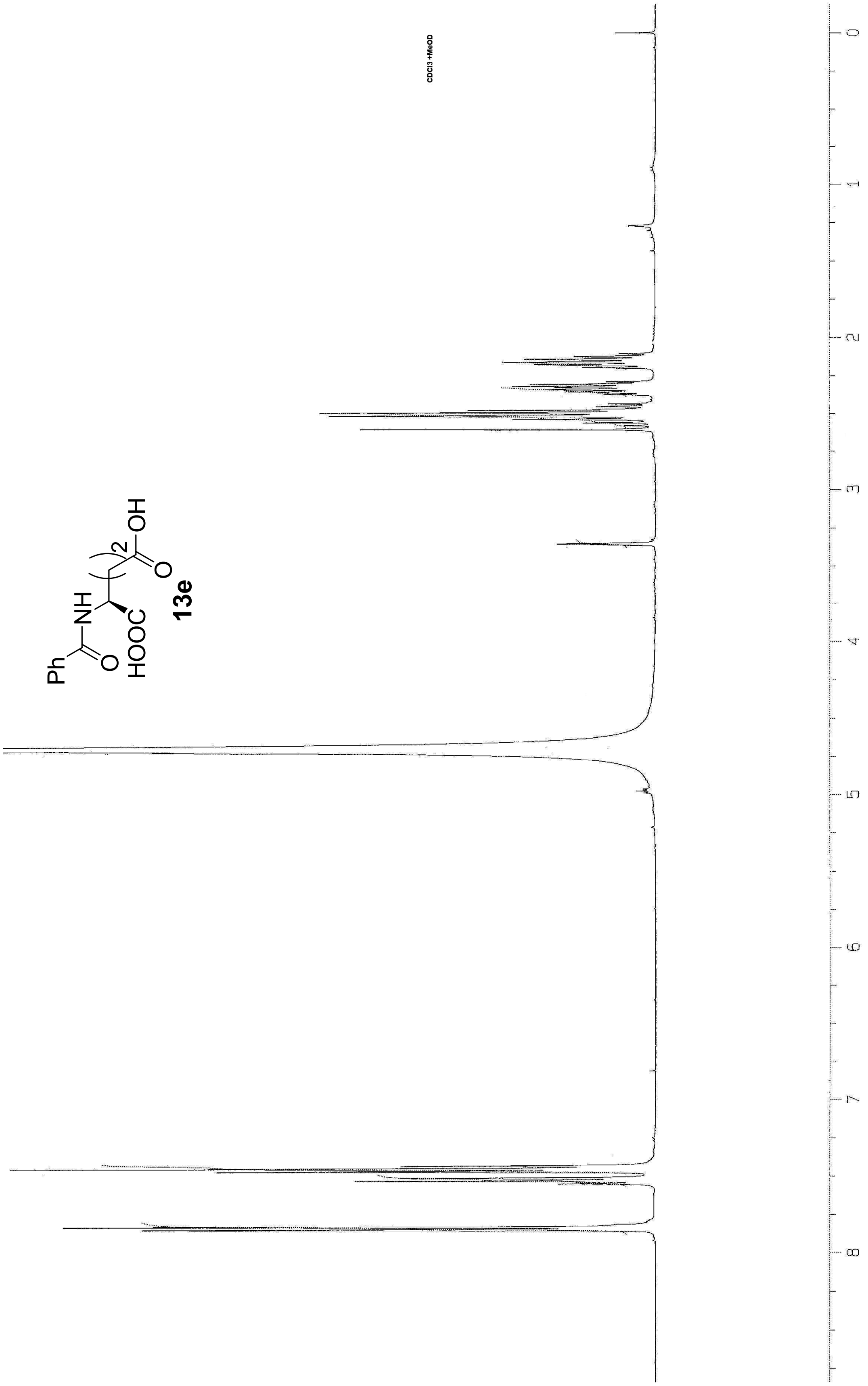

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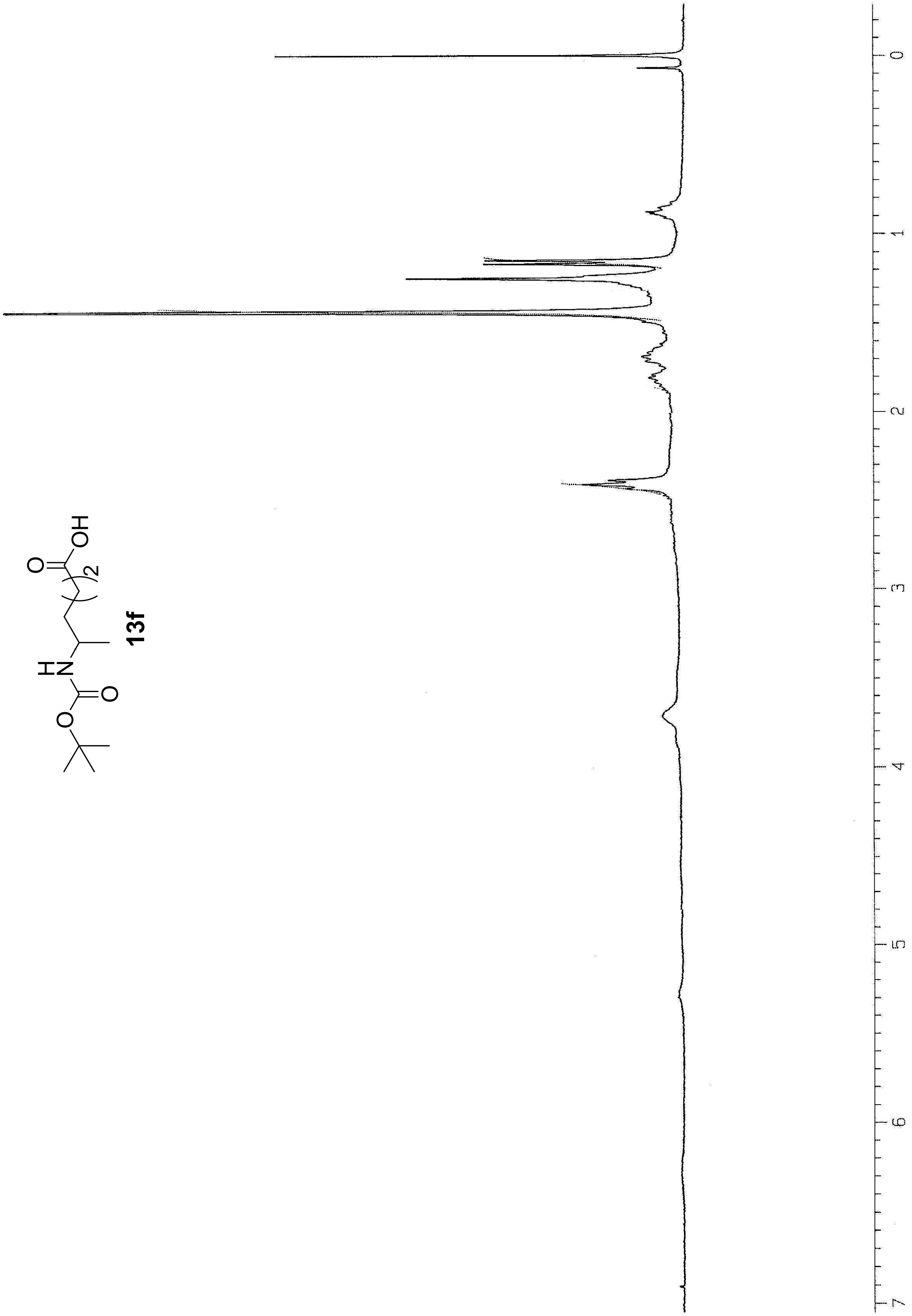

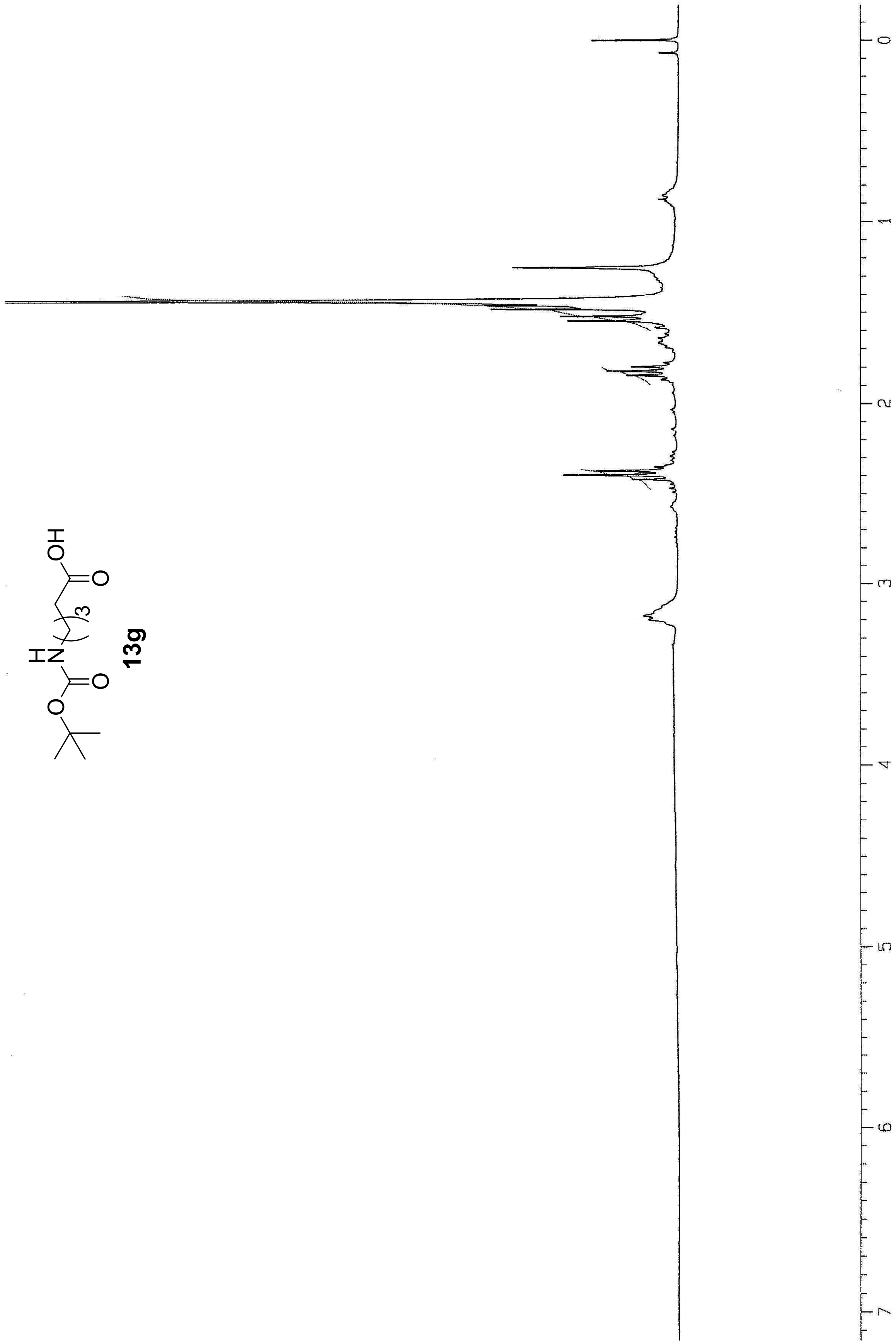

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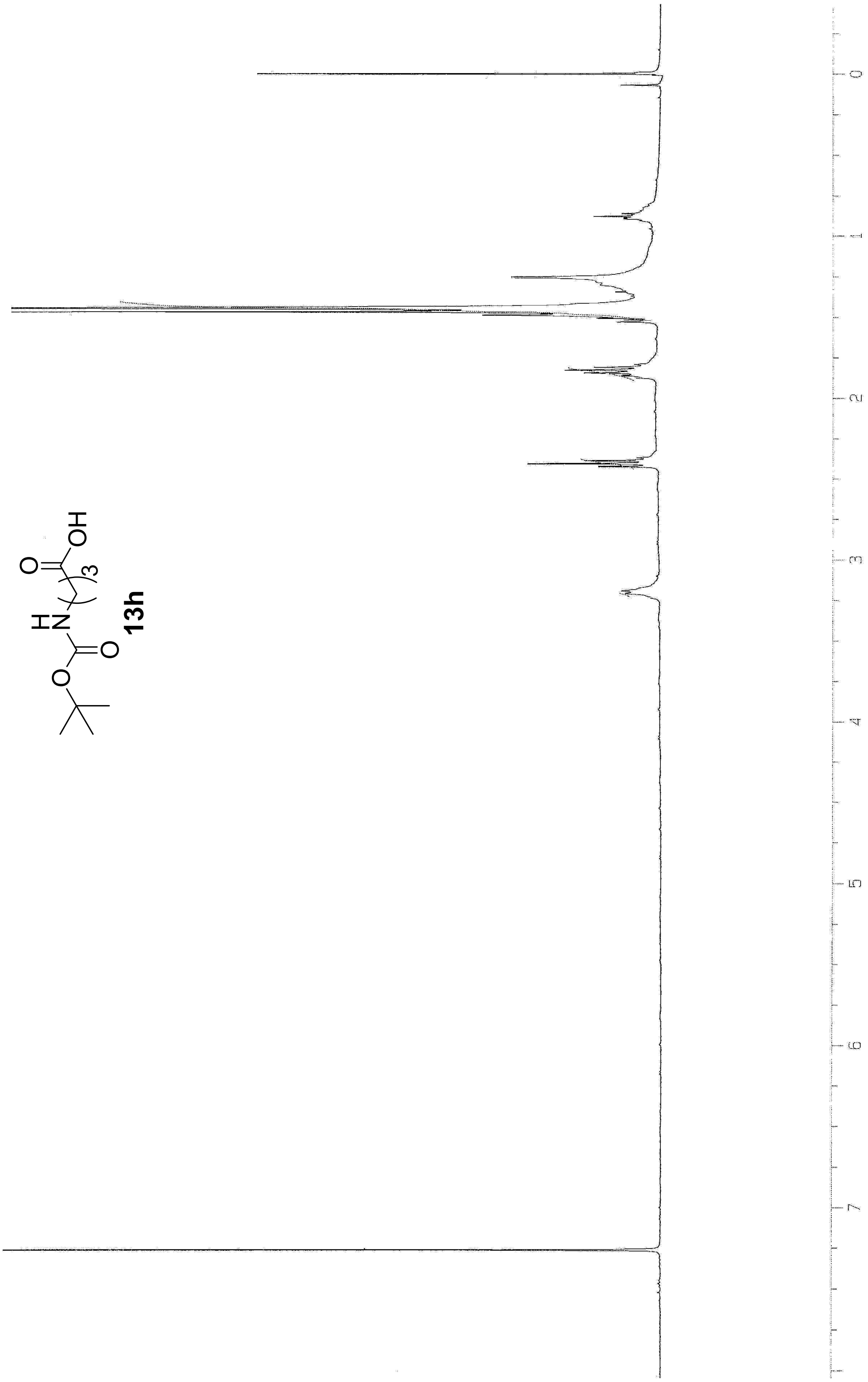

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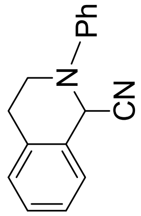

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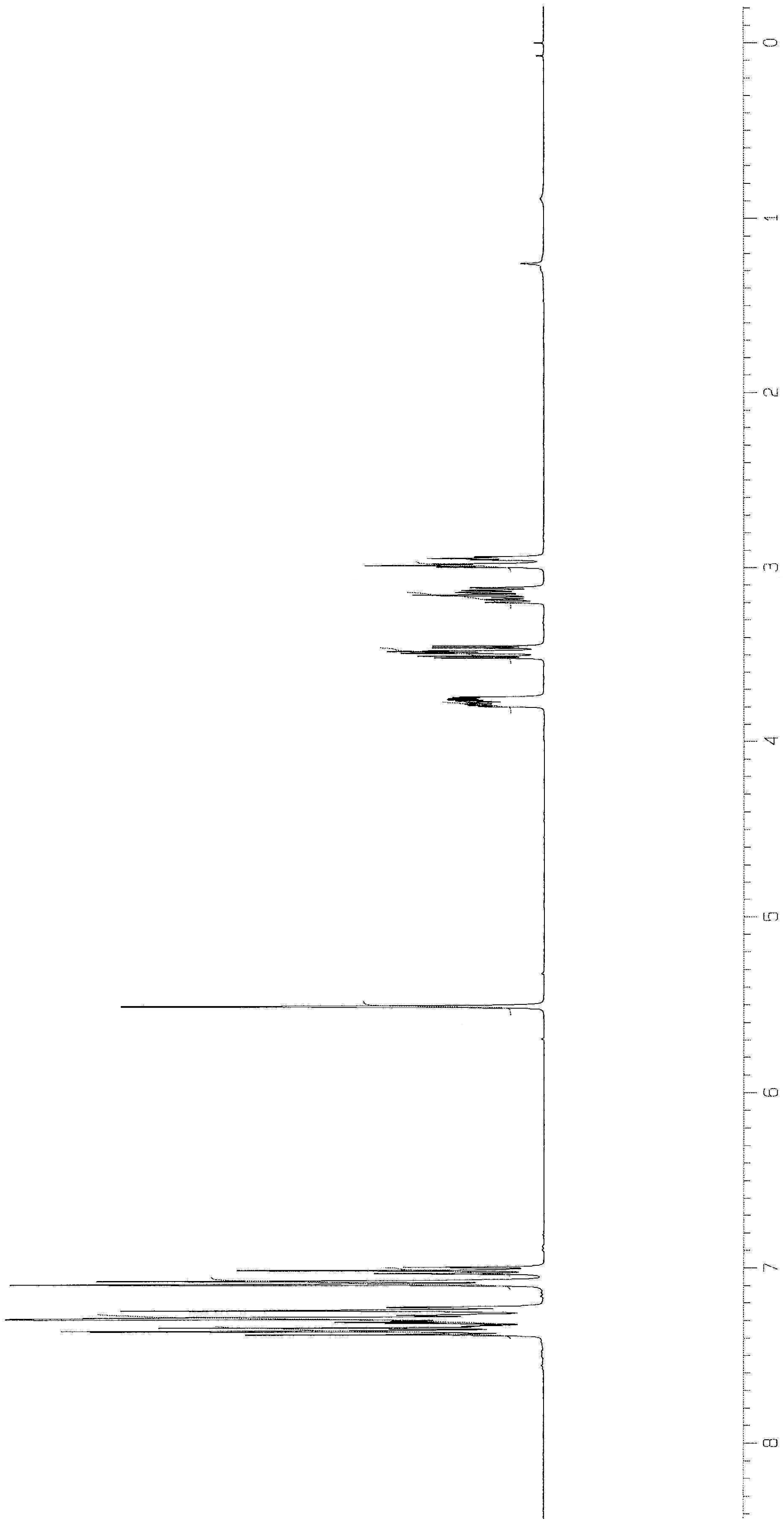

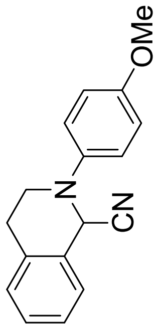

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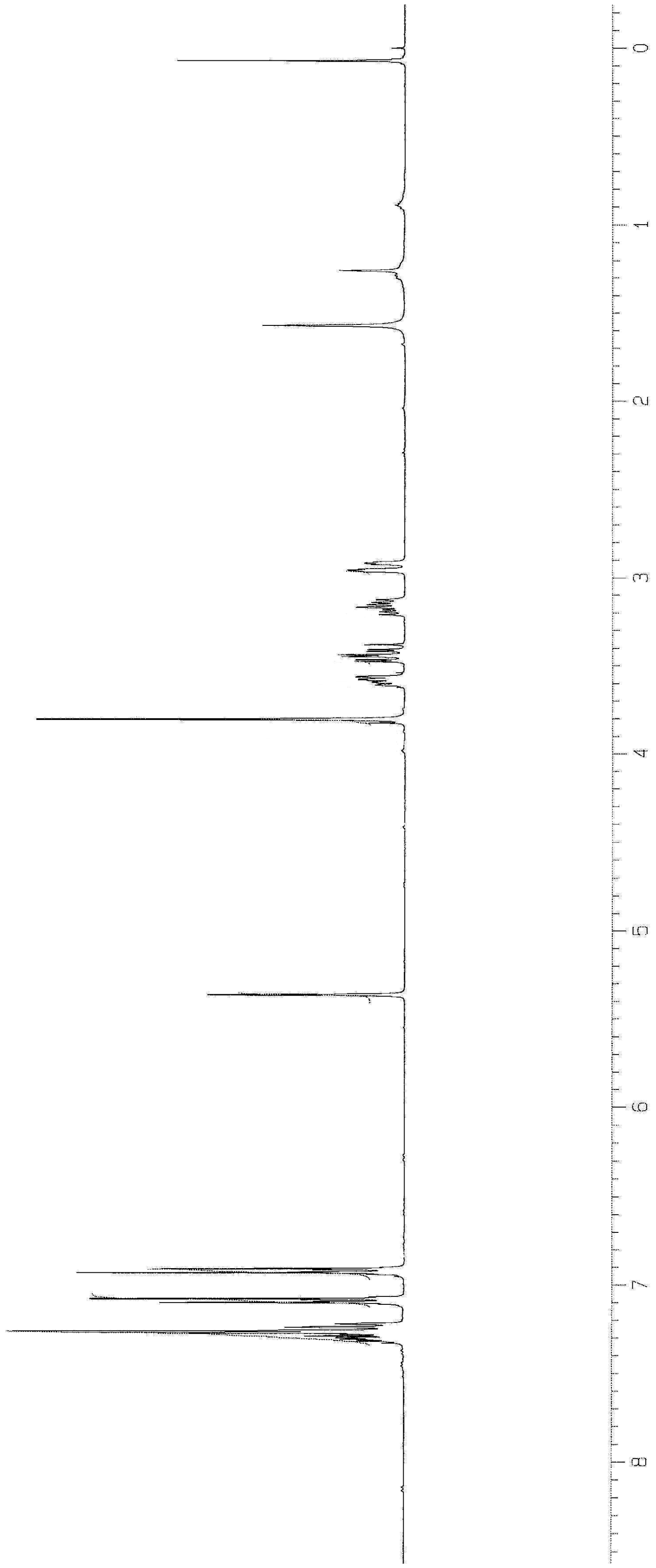

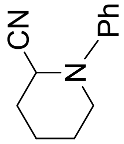

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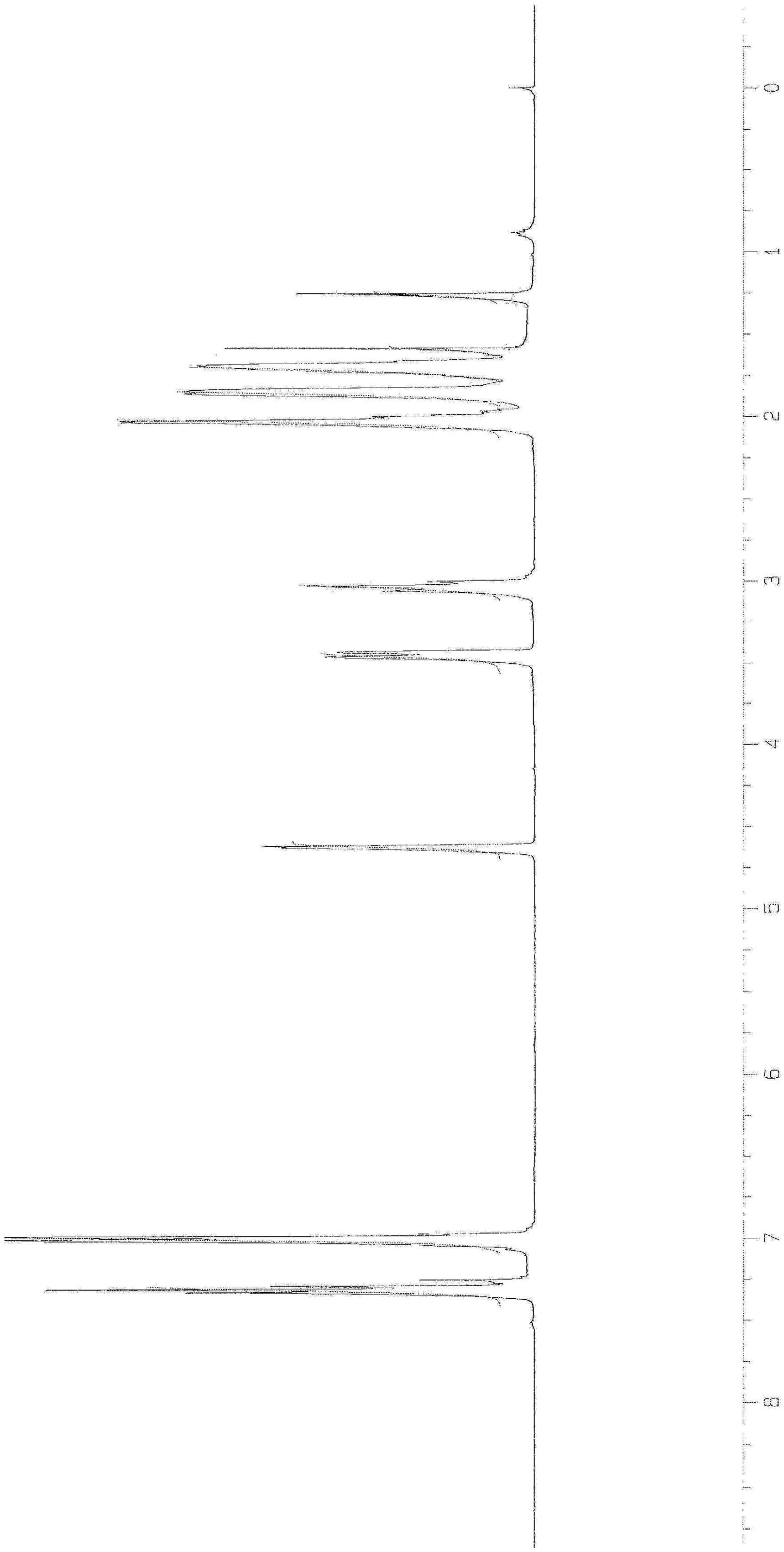

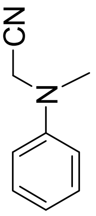

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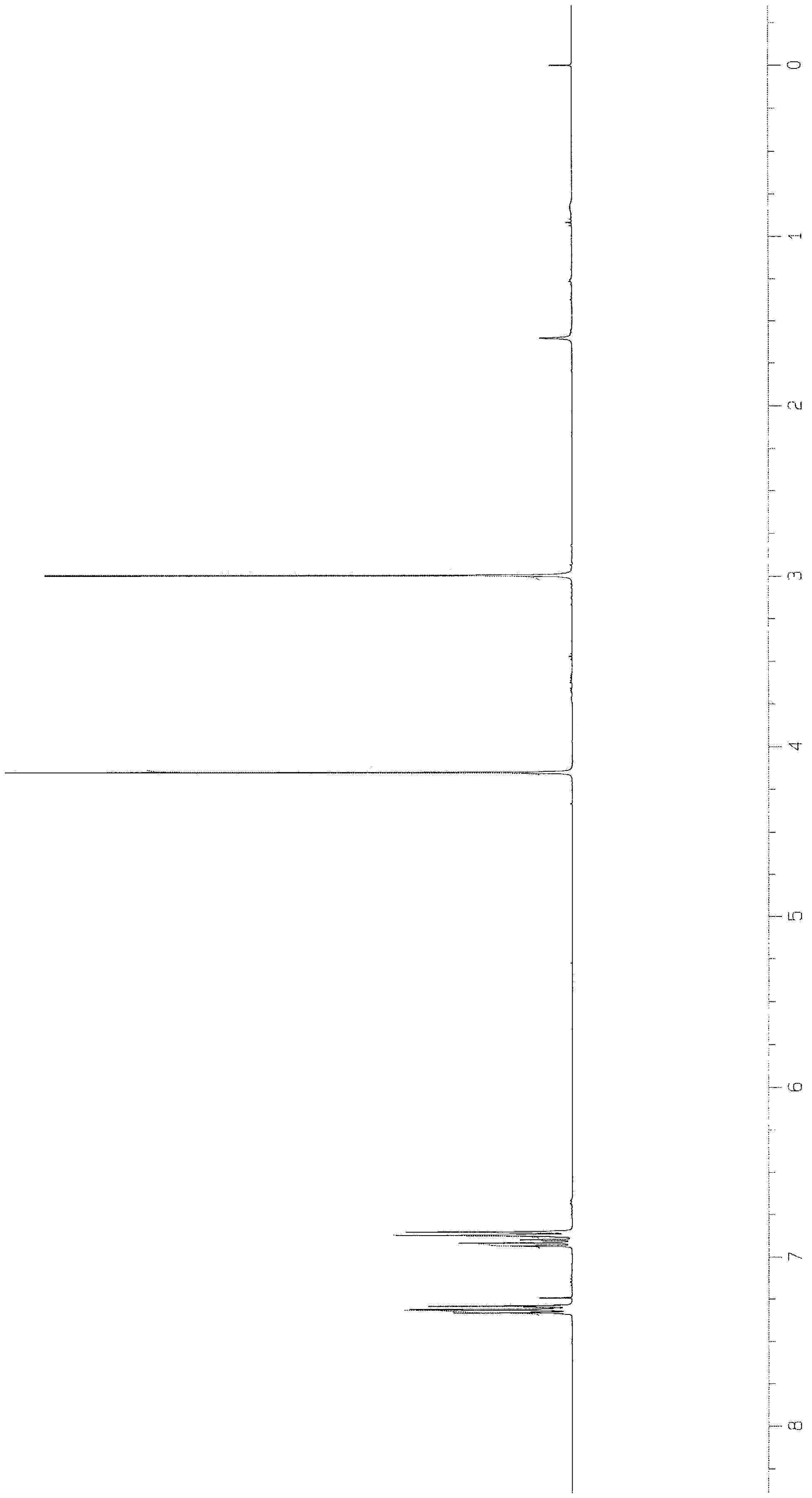

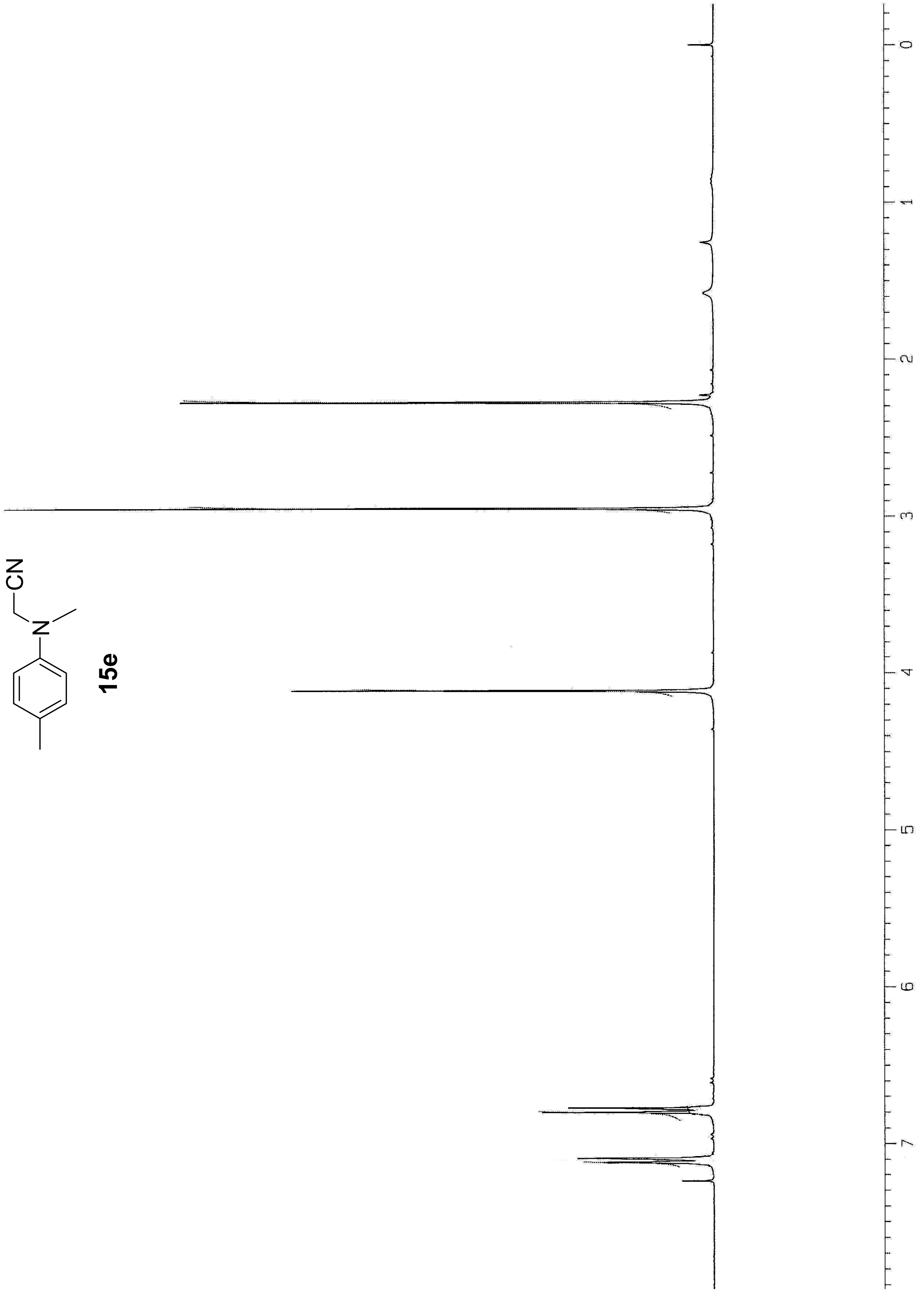

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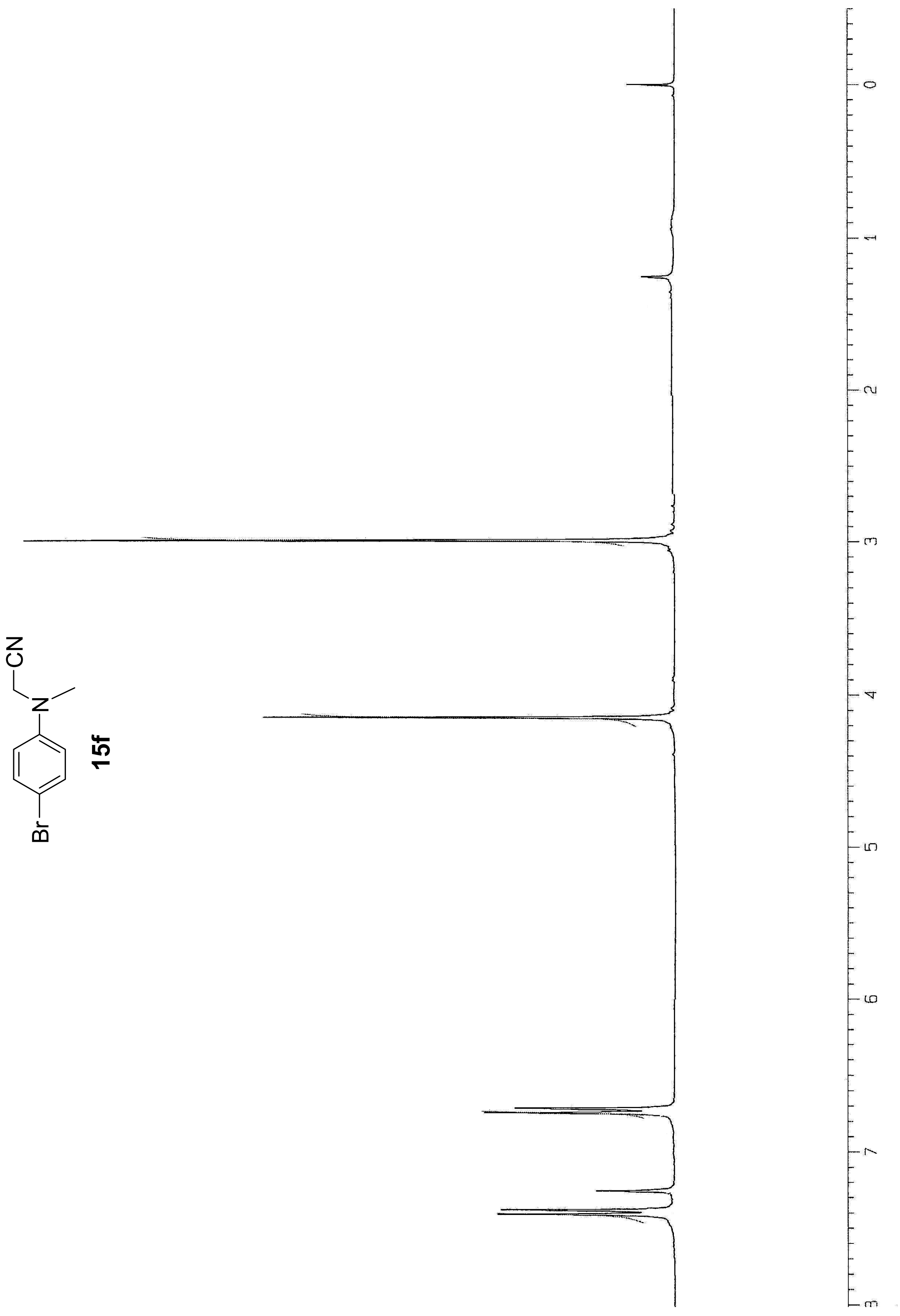

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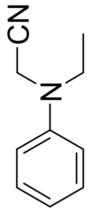

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