

Rapid and High-Yield Synthesis of [23]Crown Ether: Applied as a Wheel Component in the Formation of Pseudo[2]rotaxane and Synthesis of [2]Catenane with a Dibenzylammonium Dumbbell

Manisha Prakashni, Rasendra Shukla, and Suvankar Dasgupta*

Department of Chemistry, National Institute of Technology Patna, Patna – 800005, India

Electronic Supplementary Information

Table of Contents

1. Nominal ESI-MS of 1:1 mixture of DBA·PF₆ & X23C7	S2
2. ¹ H NMR spectrum of 1:1 mixture of DBA·PF₆ & X23C7	S3
3. Tabulation of K _a for pseudorotaxanes involving DBA⁺ & crown ethers.....	S4
4. 2D NOESY NMR spectrum of 1-H·PF₆ in CDCl ₃	S5
5. VT NMR spectrum of 1-H·PF₆ in DMSO-d ₆	S6
6. References.....	S7
7. ¹ H NMR and ¹³ C NMR spectra of key compounds.....	S8

1. Nominal ESI-MS of 1:1 mixture of DBA·PF₆ & X23C7

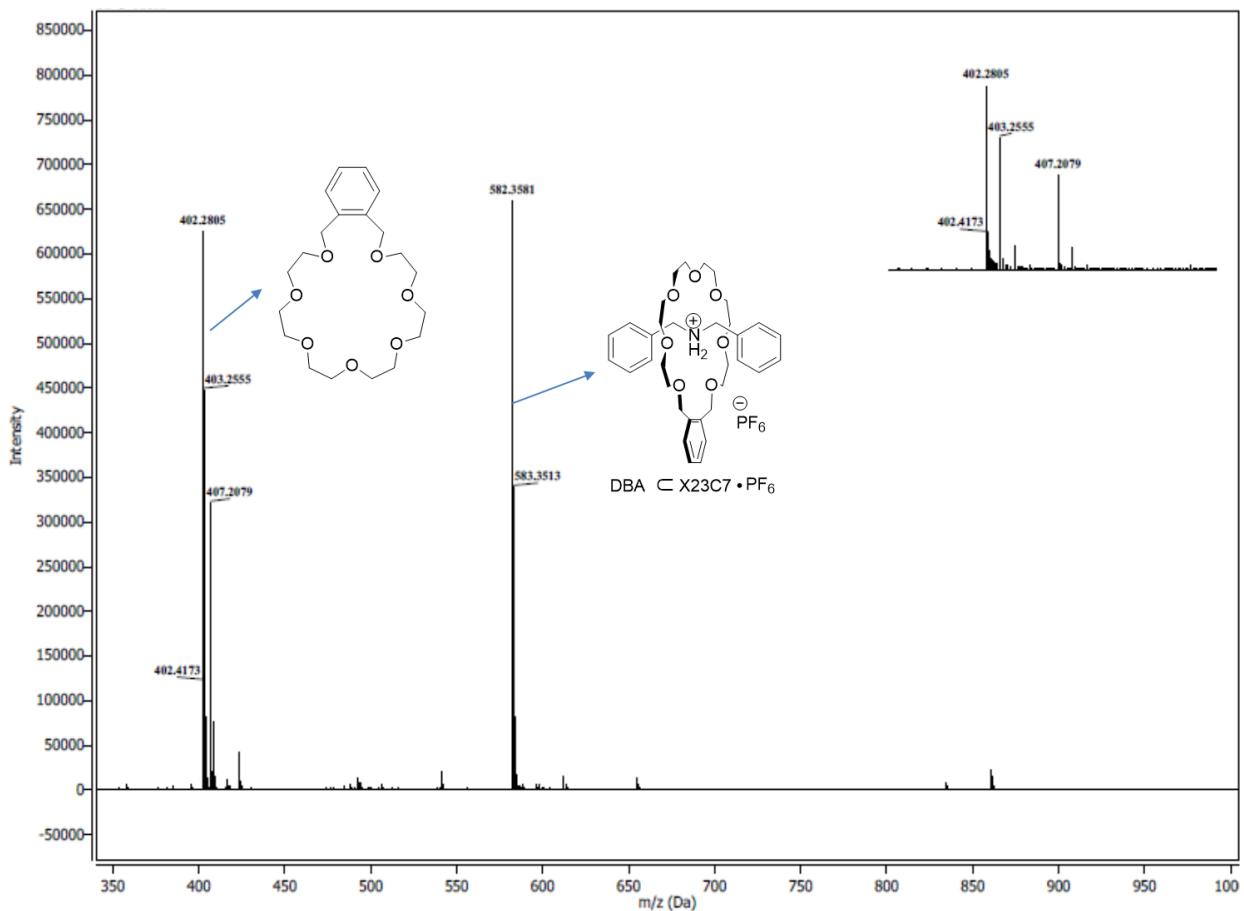


Figure S1. ESI mass spectrum of the equimolar mixture of **DBA·PF₆** & **X23C7** displayed base peak at m/z = 582.3 [M-PF₆]⁺, where “M” corresponds to the pseudo[2]rotaxane **DBA⊂X23C7·PF₆**. Strong peak was observed as well at m/z = 402.2 [M+NH₄]⁺, where “M” corresponds to the crown ether **X23C7**.

2. ^1H NMR spectrum of 1:1 mixture of DBA·PF₆ & X23C7

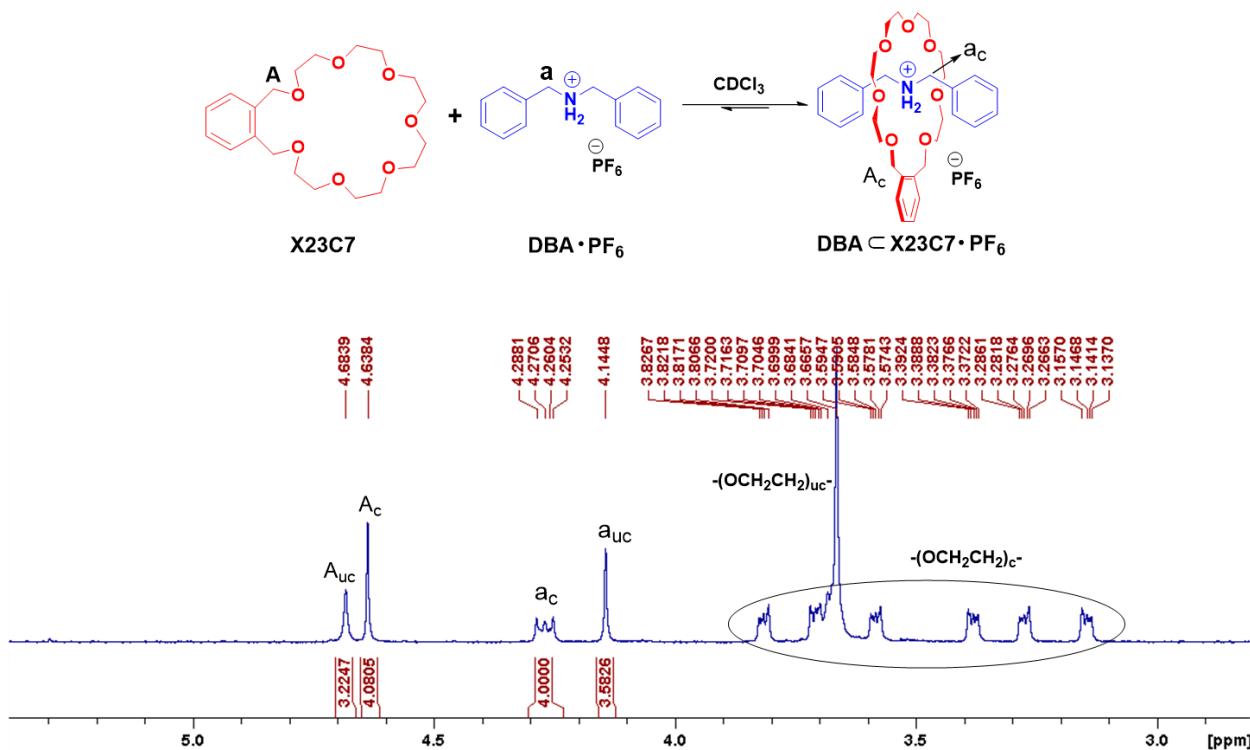


Figure S2. ^1H NMR spectrum (400 MHz, CDCl_3) of the equimolar mixture of 1.00 mM **DBA·PF₆** & **X23C7**. K_a value calculated from integrations of complexed and uncomplexed peaks “A” of **X23C7** is $[(4.0805/7.3052) \times 1.00 \times 10^{-3}] / [(1-4.0805/7.3052) \times 1.00 \times 10^{-3}]^2 = 2.86 \times 10^3 \text{ M}^{-1}$. Similarly, the K_a value calculated from integrations of complexed and uncomplexed peaks “a” of **DBA·PF₆** is $[(4.0000/7.5826) \times 1.00 \times 10^{-3}] / [(1-4.0000/7.5826) \times 1.00 \times 10^{-3}]^2 = 2.36 \times 10^3 \text{ M}^{-1}$. Therefore, the association constant for the pseudo[2]rotaxane **DBA} \subset \text{X23C7}\cdot\text{PF}_6**, $K_a = [(2.36+2.86)/2] \times 10^3 \text{ M}^{-1} = 2.61 \times 10^3 \text{ M}^{-1}$.

3. Tabulation of K_a for pseudorotaxanes involving DBA⁺ & crown ethers

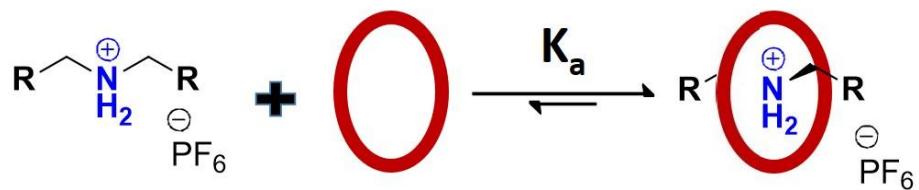


Table S1. Effect of varied cavity sized crown ethers on its association constant with dibenzylammonium ion in non-polar medium

S. No.	R	Crown Ether	Solvent	$K_a (\text{M}^{-1})$	Reference
1	Ph	X23C7	CDCl_3	2.6×10^3	This work
2	Ph	23C7H2	CDCl_3	4.6×10^3	1
3	Ph	23C6H2	CDCl_3	2.8×10^3	1
4	Ph	DB24C8	CDCl_3	2.7×10^4	2
5	Ph	ⁱ DB24C8	CDCl_3	2.2×10^4	3
6	<i>p</i> -(CO ₂ Me)Ph	BMP25C8	CD_2Cl_2	50	4
7	Ph	BMP26C8	CDCl_3	0	5
8	Ph	TB27C9	3:1 ($\text{CDCl}_3:\text{CD}_3\text{CN}$)	270	6

Note: **23C7H2** = 23-crown-7; **23C6H2** = 23-crown-6; **DB24C8** = Dibenzo-24-crown-8; **ⁱDB24C8** = *iso*-Dibenzo-24-crown-8; **BMP25C8** = Benzometaphenylene-25-crown-8; **BMP26C8** = Bismetaphenylene-26-crown-8; **TB27C9** = Tribenzo-27-crown-9.

4. 2D NOESY NMR spectrum of **1-H·PF₆** in CDCl₃

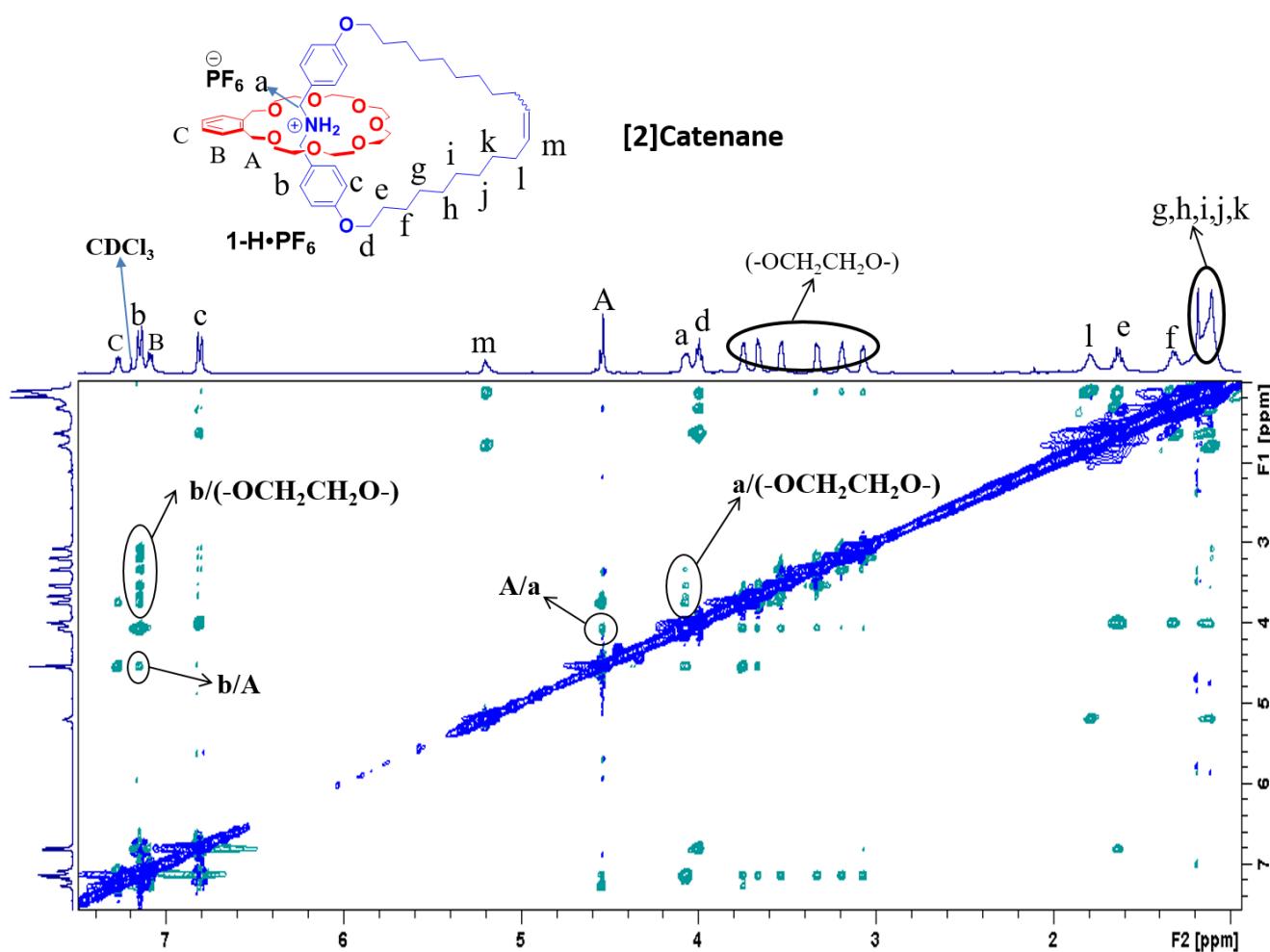


Figure S3. 2D NOESY ¹H NMR spectrum (400 MHz) of **1-H·PF₆** in CDCl₃. NOESY spectra correlates protons not separated by more than 5 Angstroms through space. In our case, we noticed a strong correlation of (-OCH₂CH₂O-) protons of **X23C7** crown ether with the protons of DBA⁺-based macrocycle (referred as “a” and “b”), decisively proving that **X23C7** crown ether indeed clipped onto the dumbbell. Moreover, there exists correlation between benzylic protons “A” of **X23C7** crown ether with the benzylic protons (a) and phenyl protons (b) of the DBA⁺-based macrocycle, further supporting our argument.

5. VT NMR spectrum of **1-H·PF₆** in DMSO-d₆

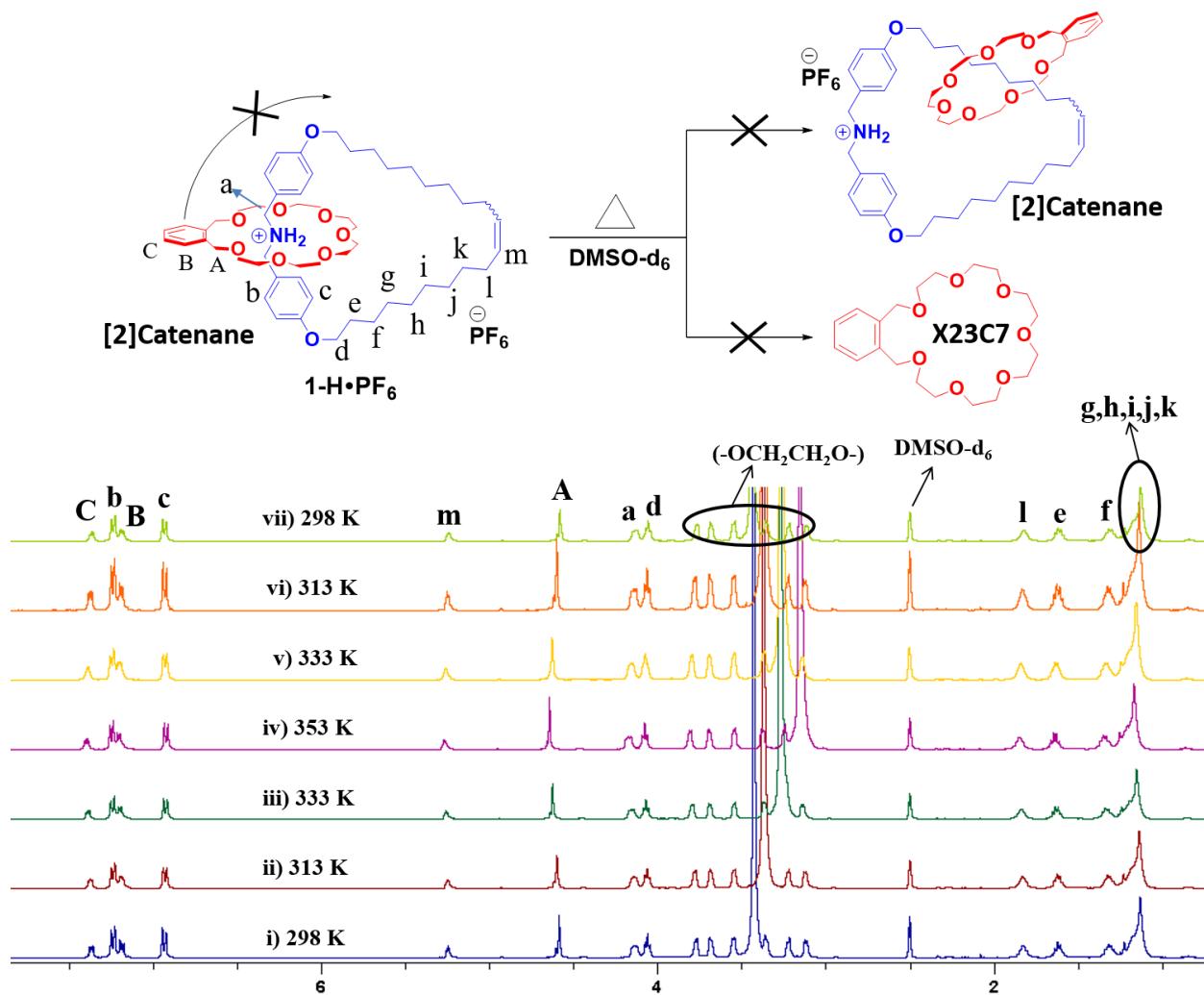
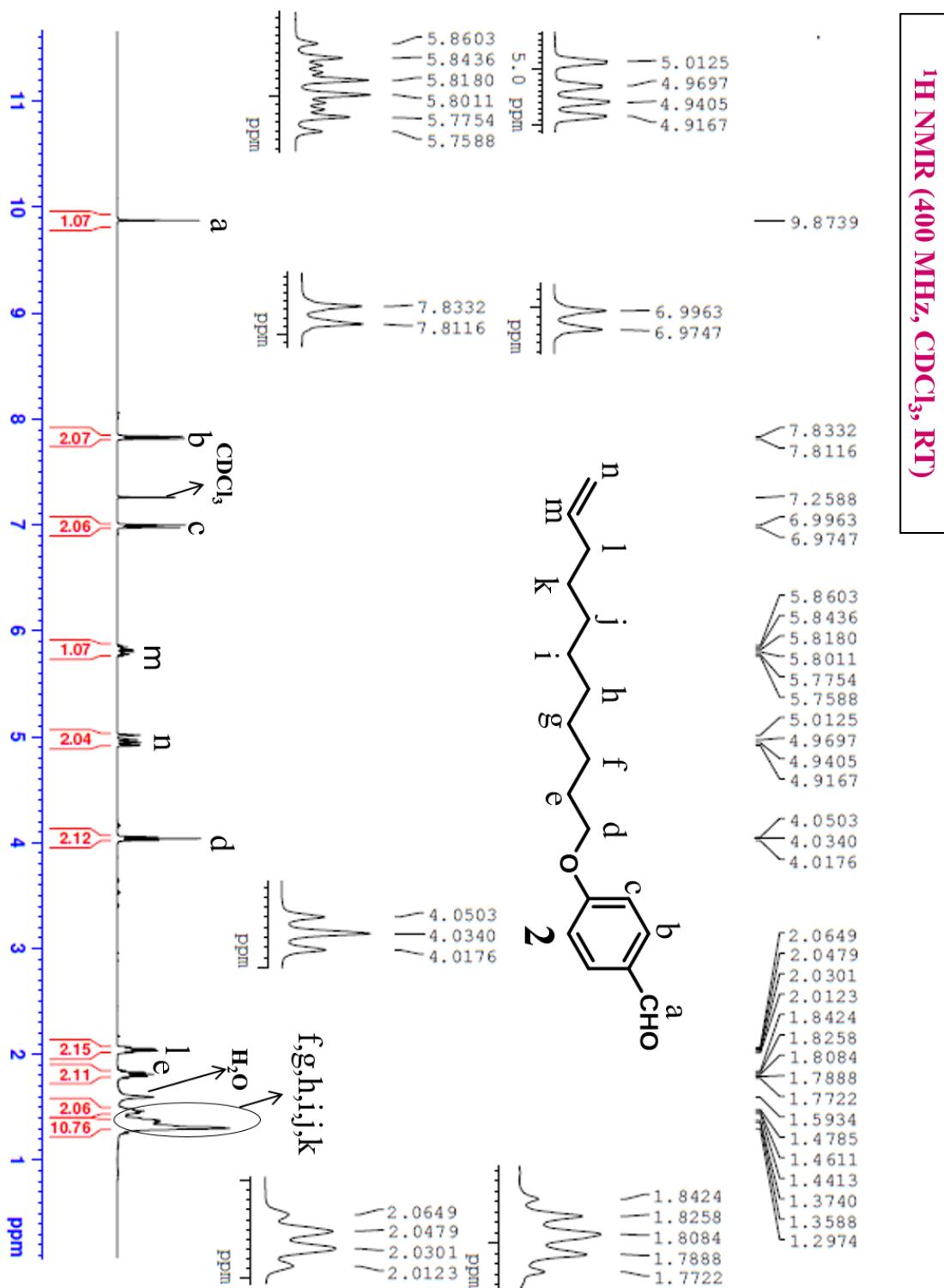


Figure S4. Stacked partial ¹H NMR spectra (400 MHz, CD₃SOCD₃) of **1-H·PF₆** at different temperatures. The peaks of interest “a” & -(OCH₂CH₂O)- did not show any shift on increasing the temperature stepwise to 353 K (i-iv), excepting the water peak. Cooling down to room temperature (iv-vii) was no different. This implies that **1-H·PF₆** is indeed kinetically interlocked species, which maintains its integrity at elevated temperature in a polar solvent. This it to say that the confirmation (X23C7 encircling DBA⁺) of **1-H·PF₆** is the thermodynamically most stable conformation, not only at room temperature but also at 353 K, even in DMSO-d₆.

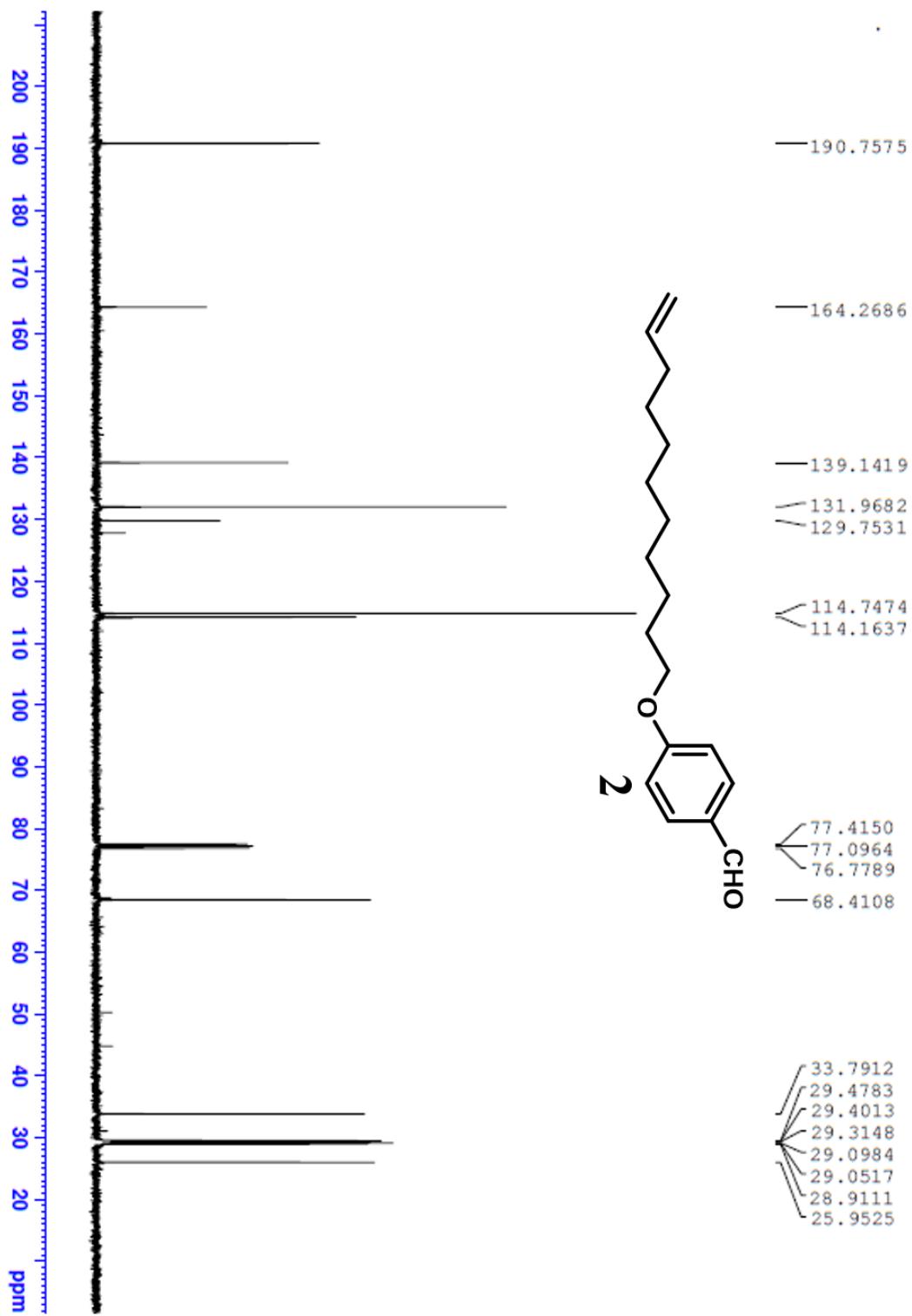
6. References

- 1) Dasgupta, S.; Wu, J. Formation of [2]Rotaxanes by Encircling [20], [21] and [22]Crown Ethers onto the Dibenzylammonium Dumbbell. *Chem. Sci.* **2012**, *3*, 425–432.
- 2) Ashton, P. R.; Campbell, P. J.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Philp, D.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; Williams, D. J. Dialkylammonium Ion/Crown Ether Complexes: The Forerunners of a New Family of Interlocked Molecules. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1865–1869.
- 3) Ashton, P. R.; Chrystal, E. J. T.; Glink, P. T.; Menzer, S.; Schiavo, C.; Spencer, N.; Stoddart, J. F.; Tasker, P. A.; White, A. J. P.; Williams, D. J. Pseudorotaxanes Formed between Secondary Dialkylammonium Salts and Crown Ethers. *Chem.-Eur. J.* **1996**, *2*, 709–728.
- 4) Cantrill, S. J.; Fulton, D. A.; Heiss, A. M.; Pease, A. R.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. The Influence of Macrocyclic Polyether Constitution upon Ammonium Ion/Crown Ether Recognition Processes. *Chem.-Eur. J.* **2000**, *6*, 2274–2287.
- 5) Bryant, W. S.; Guzei, I. A.; Rheingold, A. L.; Merola, J. S.; Gibson, H. W. A Study of the Complexation of Bis(m-Phenylene) Crown Ethers and Secondary Ammonium Ions. *J. Org. Chem.* **1998**, *63*, 7634–7639.
- 6) Cantrill, S. J.; Fyfe, M. C. T.; Heiss, A. M.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. Tribenzo[27]Crown-9: A New Ring for Dibenzylammonium Rods. *Org. Lett.* **2000**, *2*, 61–64.

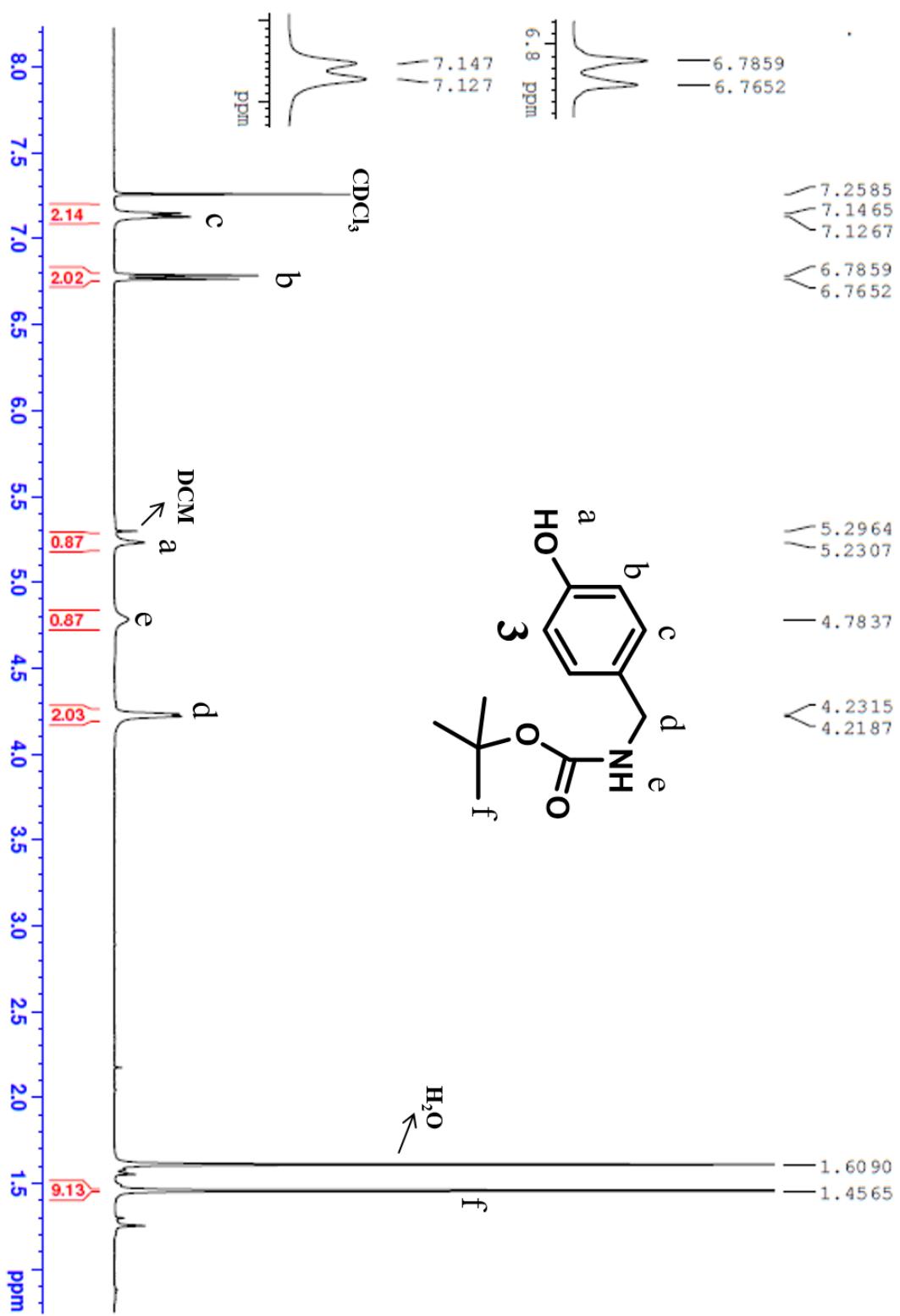
7. ^1H NMR and ^{13}C NMR spectra of key compounds



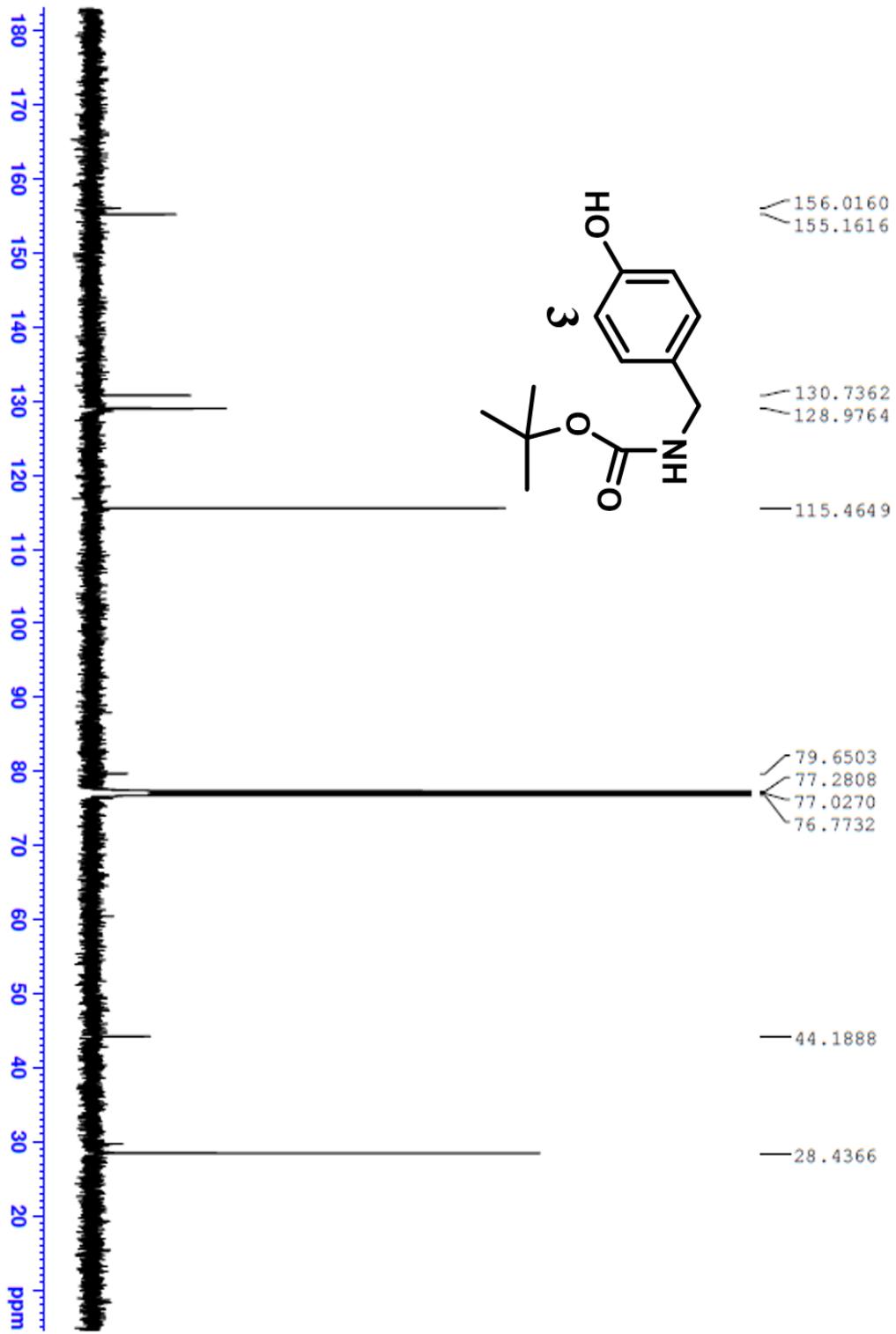
$^{13}\text{C}\{{}^1\text{H}\}$ NMR (100 MHz, CDCl_3 , RT)



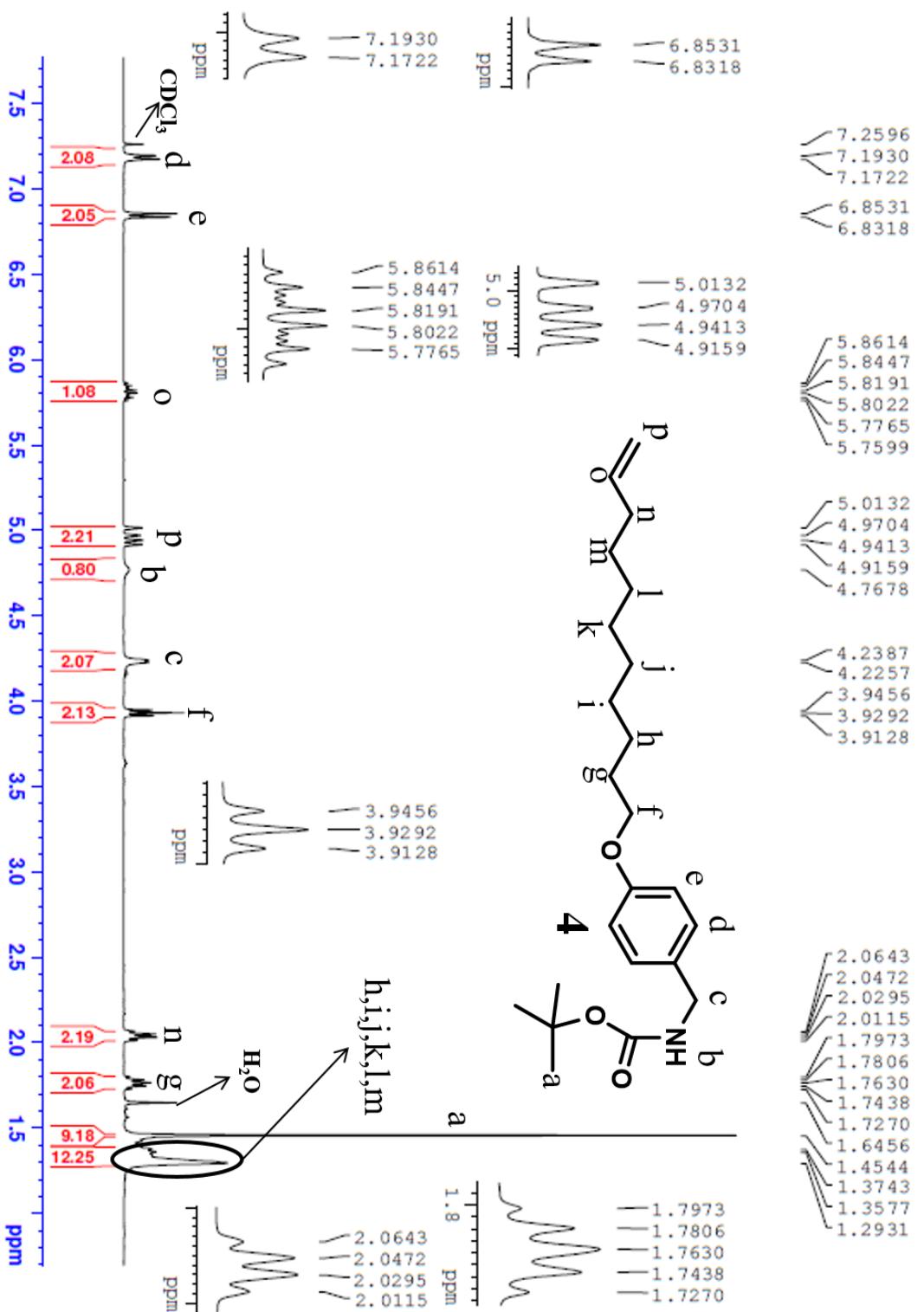
¹H NMR (400 MHz, CDCl₃, RT)



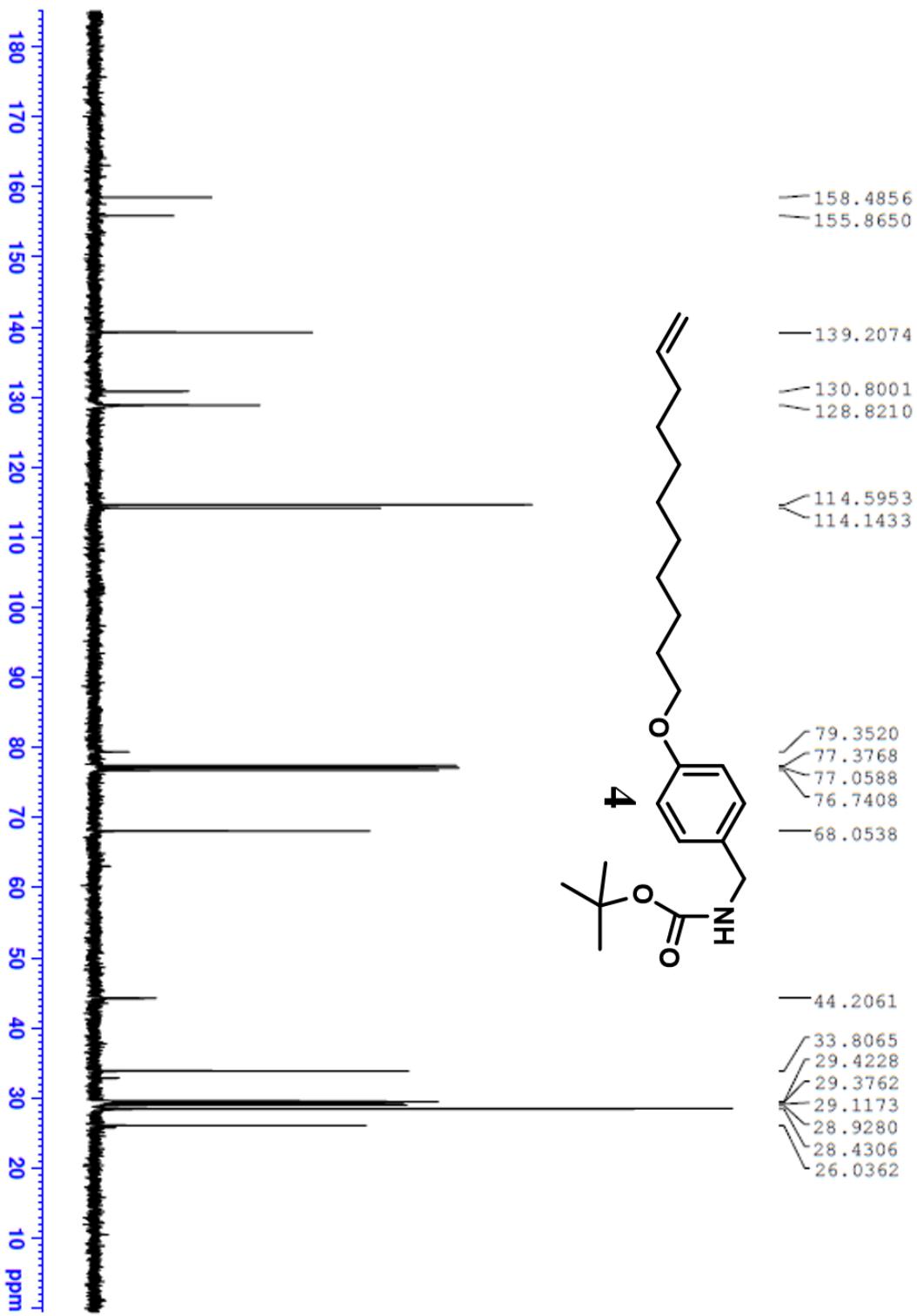
¹³C{¹H} NMR (125 MHz, CDCl₃, RT)



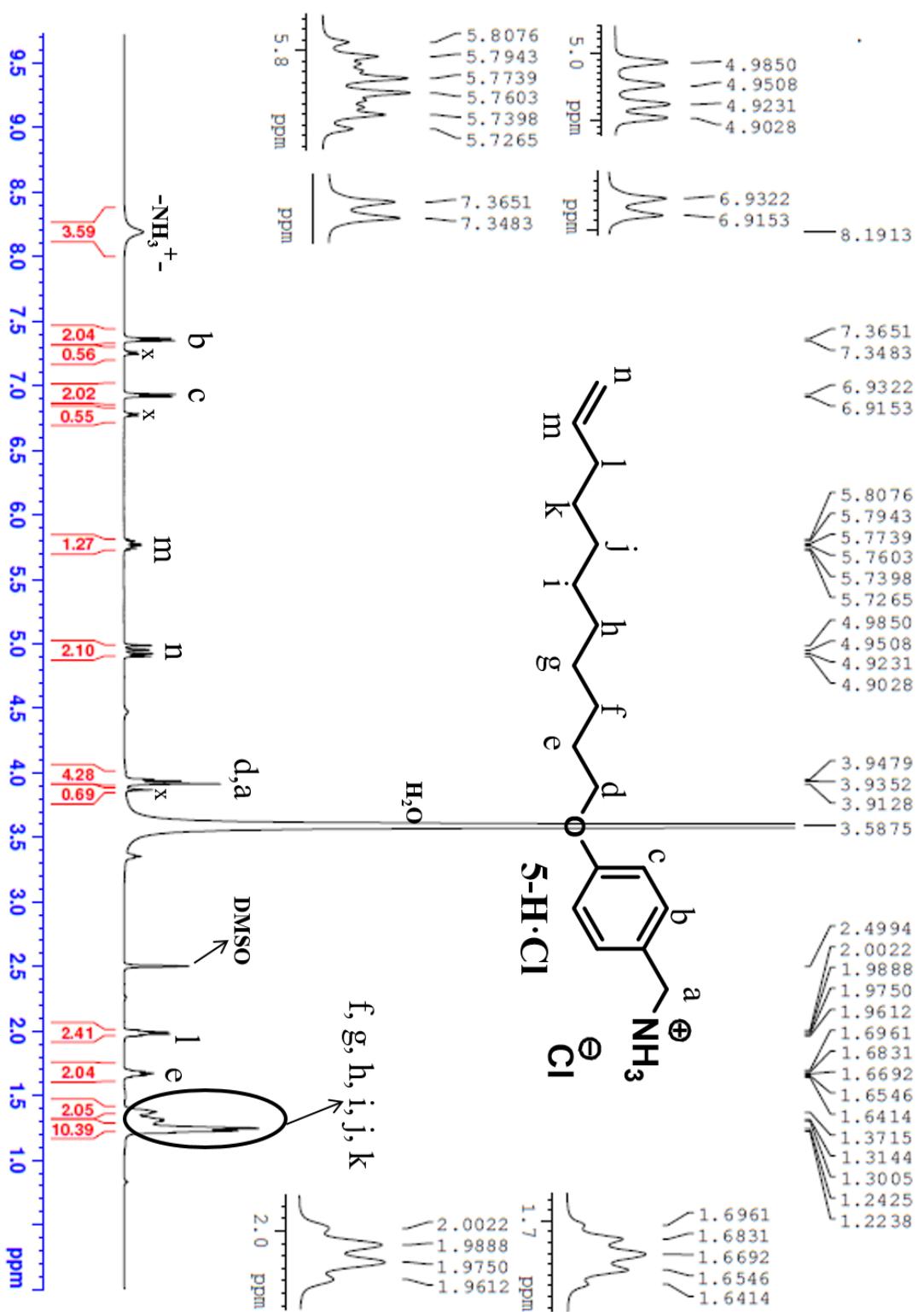
¹H NMR (400 MHz, CDCl₃, RT)



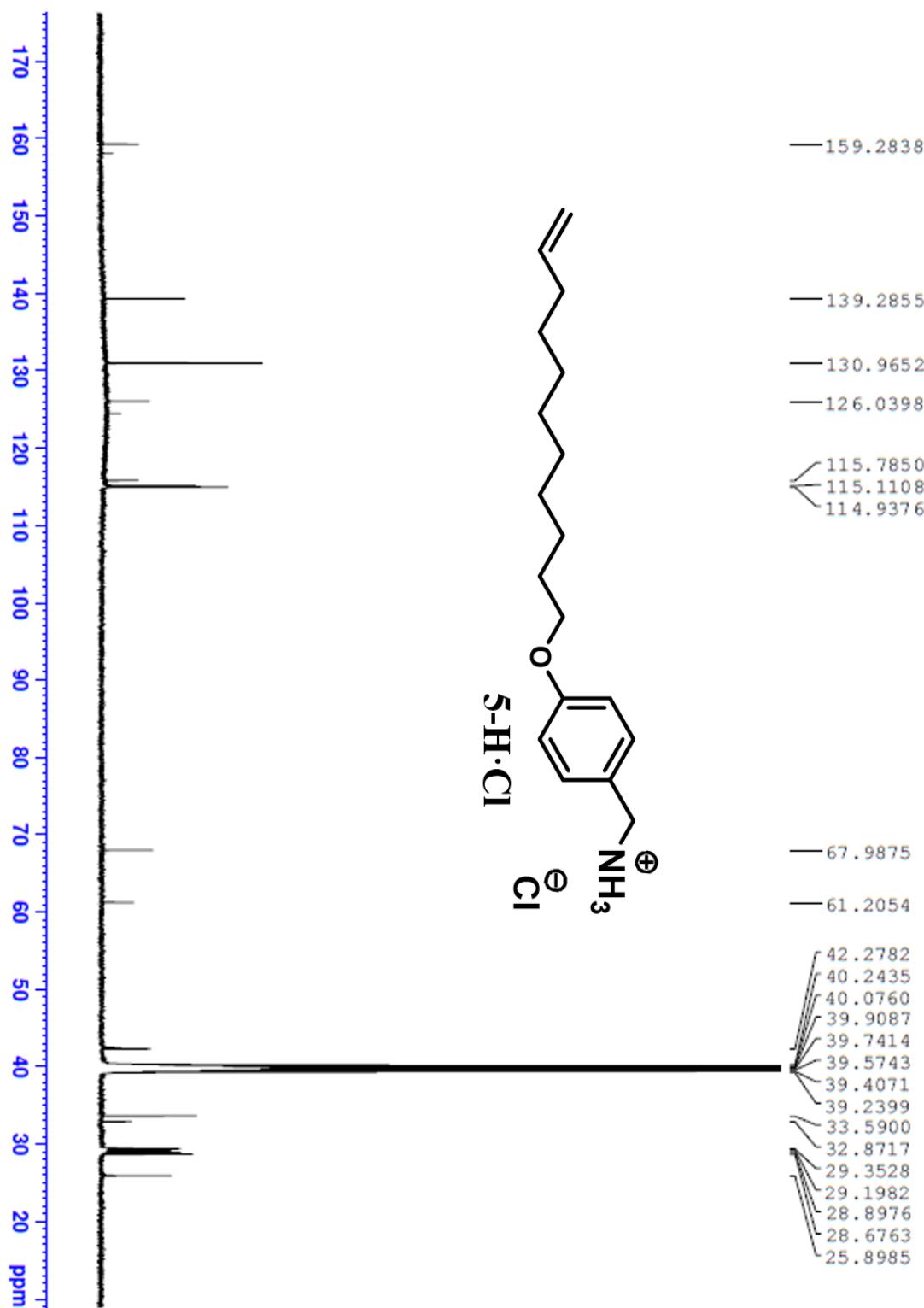
¹³C{¹H} NMR (100 MHz, CDCl₃, RT)



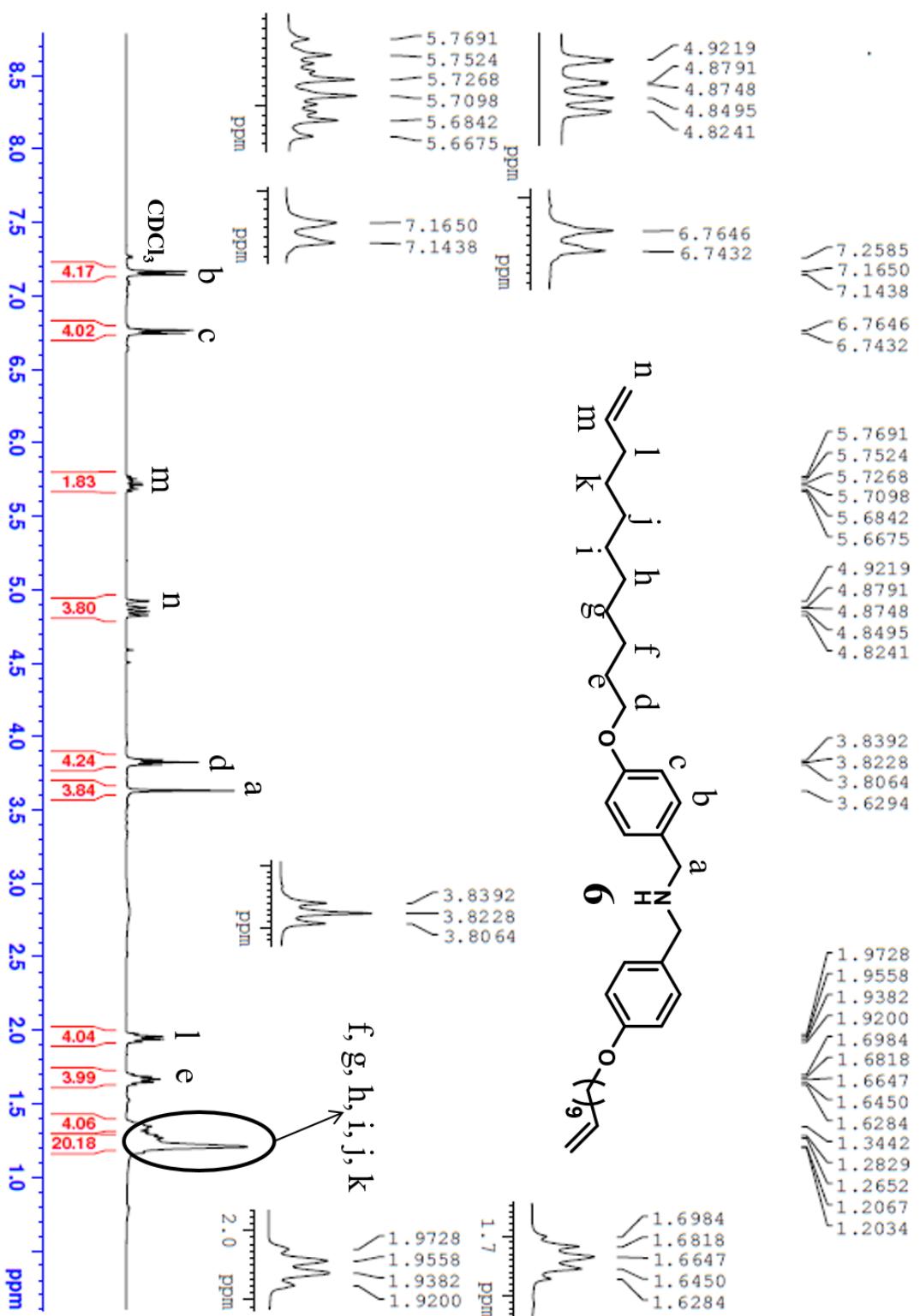
¹H NMR (500 MHz, DMSO, RT)



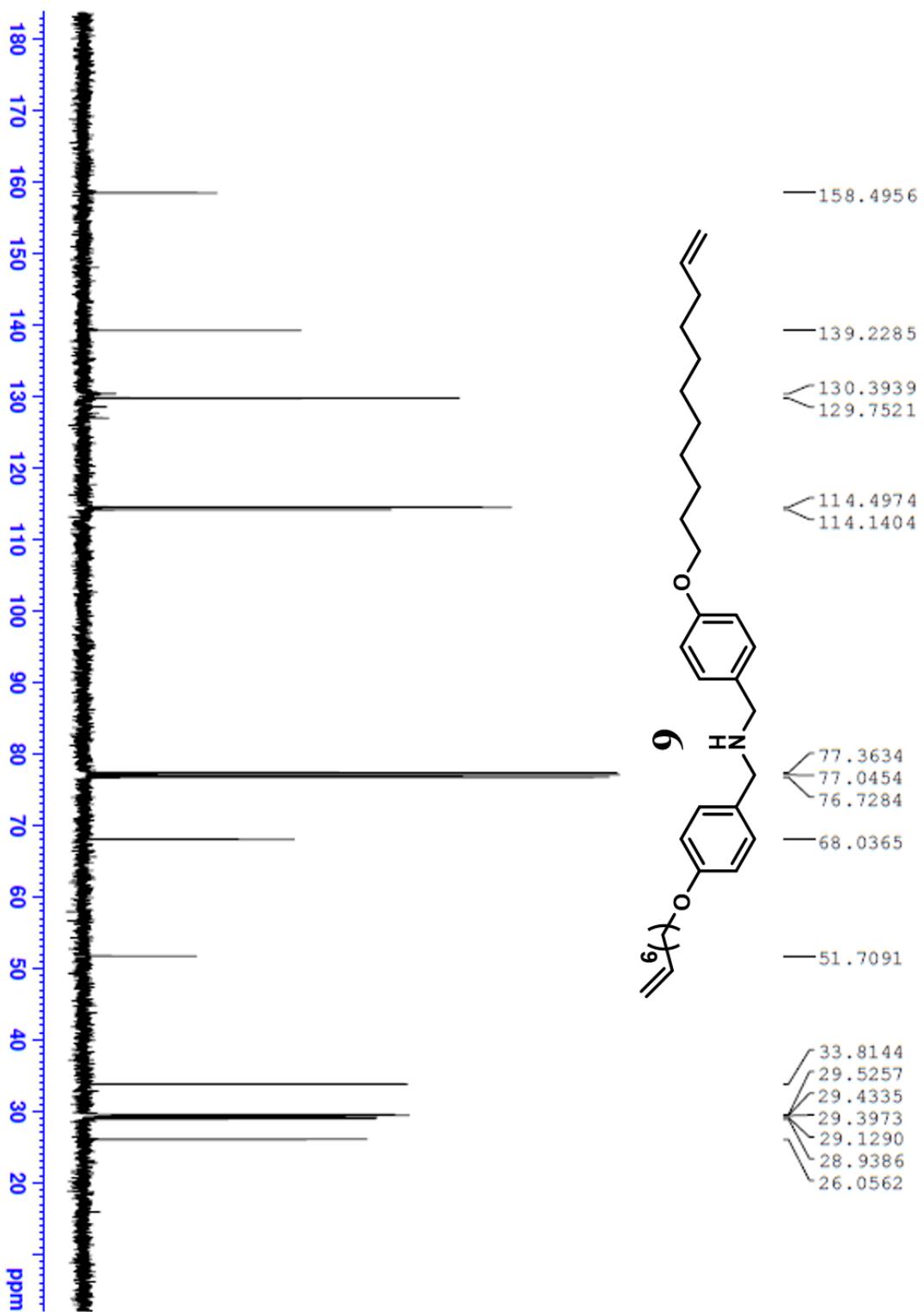
$^{13}\text{C}\{\text{H}\}$ NMR (125 MHz, DMSO, RT)



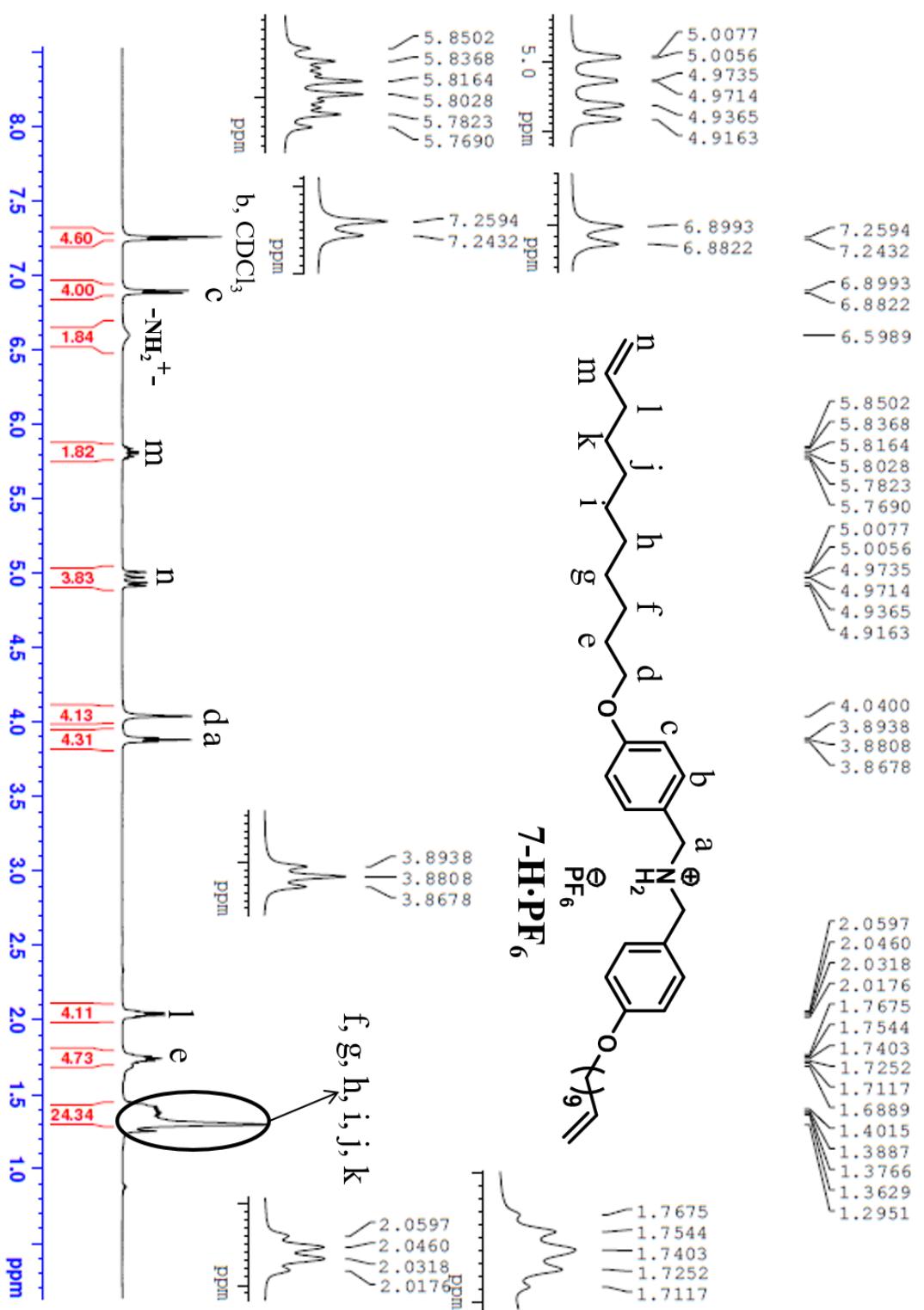
¹H NMR (400 MHz, CDCl₃, RT)



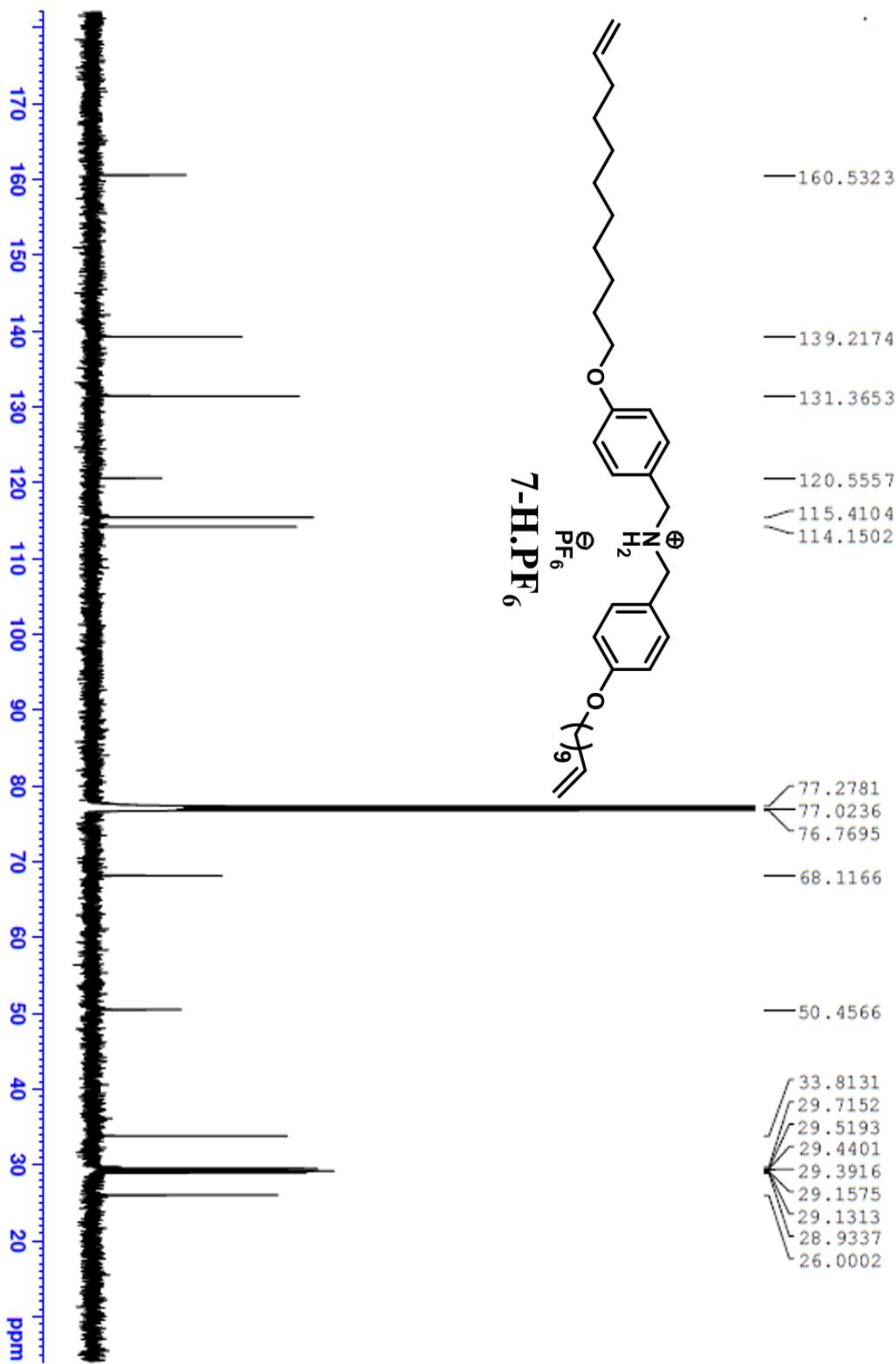
¹³C{¹H} NMR (100 MHz, CDCl₃, RT)



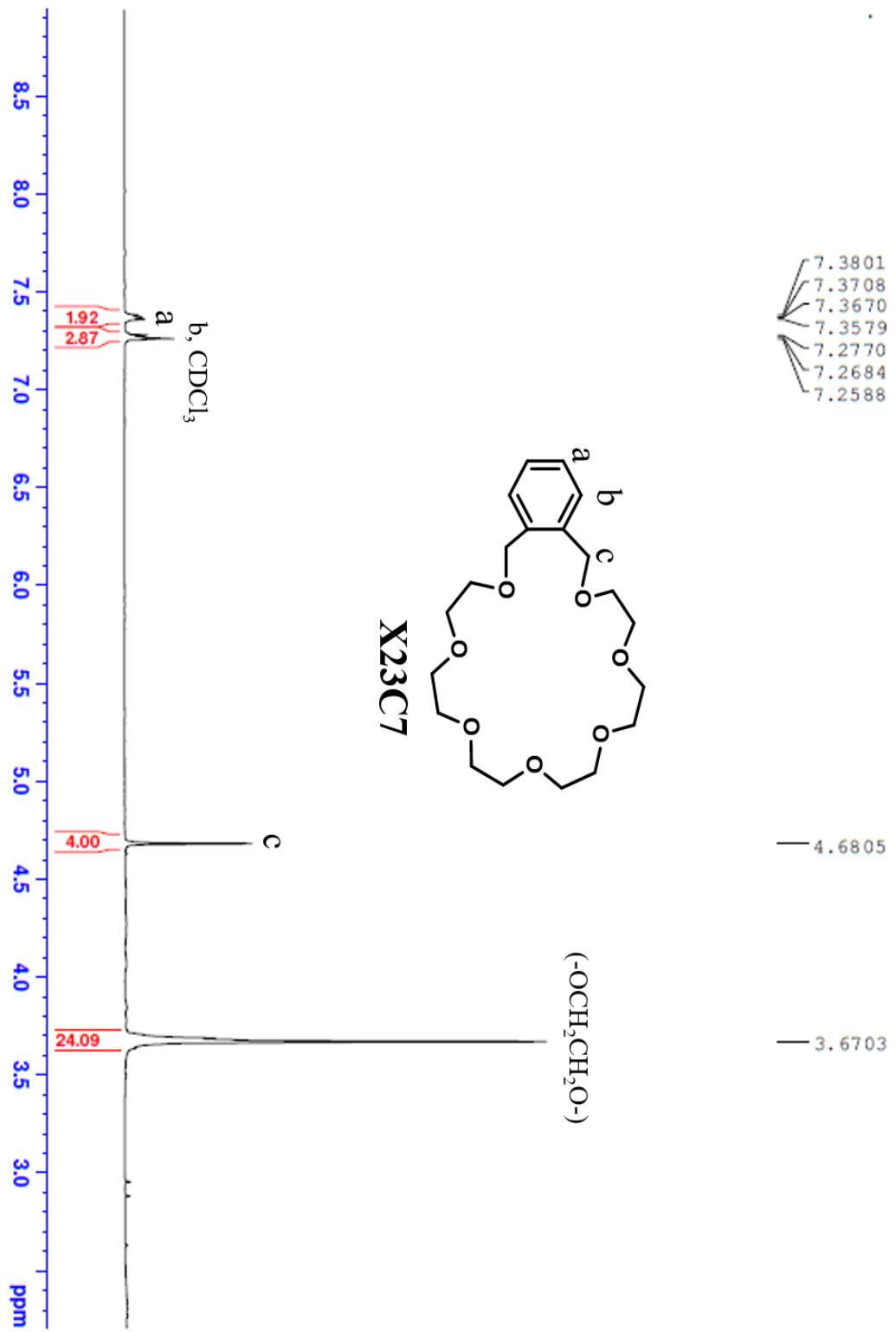
¹H NMR (500 MHz, CDCl₃, RT)



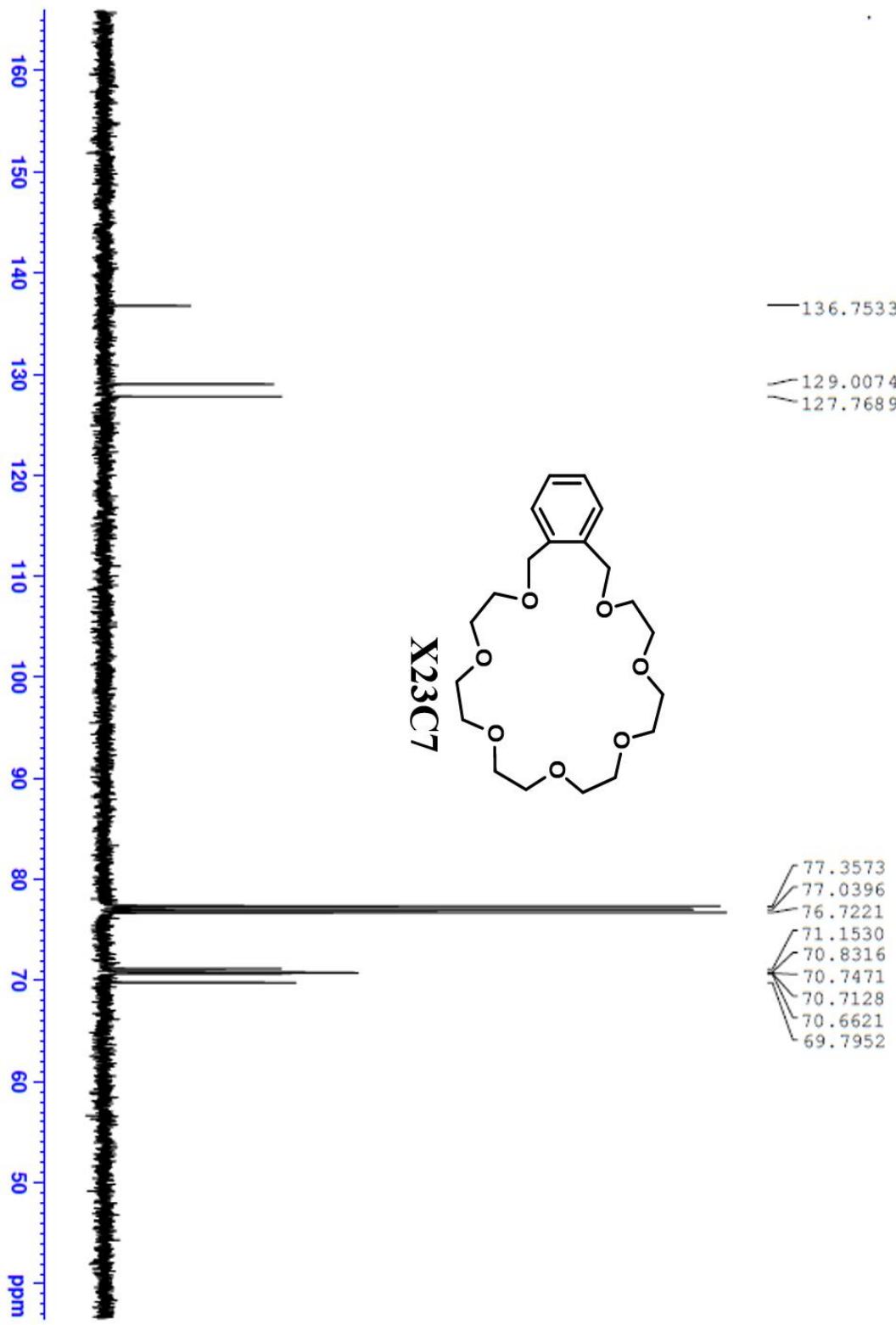
¹³C{¹H} NMR (125 MHz, CDCl₃, RT)



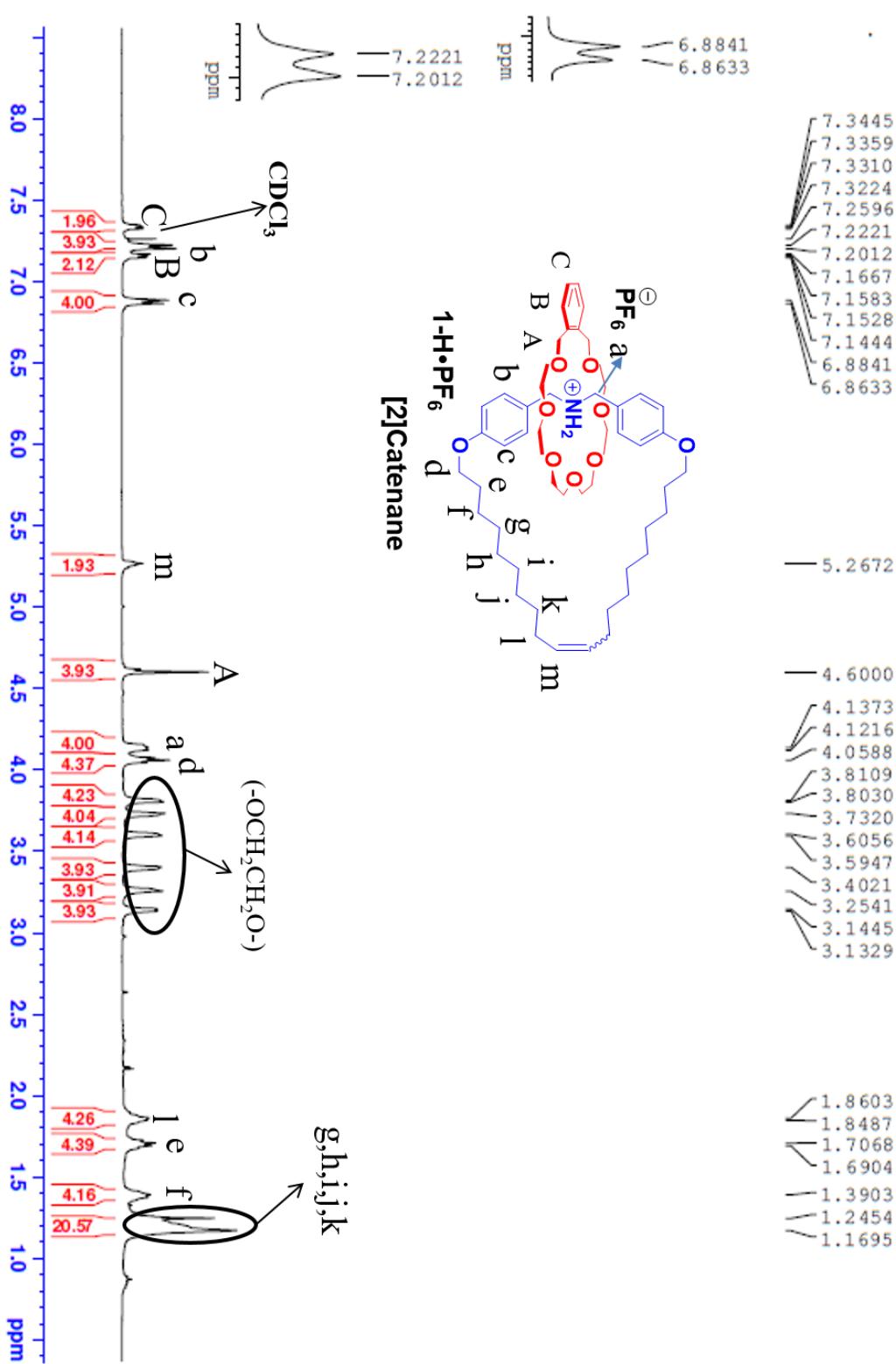
¹H NMR (400 MHz, CDCl₃, RT)



$^{13}\text{C}\{{}^1\text{H}\}$ NMR (100 MHz, CDCl_3 , RT)



¹H NMR (400 MHz, CDCl₃, RT)



$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3 , RT)

