One-handed Helical Polynorbornene Having Aza-18-crown-6 Pendants Induced by Protonated Amino Acids

Renjie Ji, Chih-Gang Chao, Yen-Chin Huang, Yi-kang Lan, Cheng-Lu Lu, and Tien-Yau Luh*

Shanghai Institute of Organic Chemistry, 354 Ling Ling Lu, Shanghai 200032, China
Department of Chemistry, National Taiwan University, Taipei, Taiwan 106
Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan 106
Fax +886-2-2364-4971, e-mail: tyluh@ntu.edu.tw

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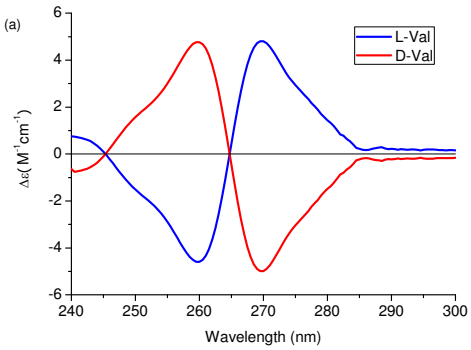
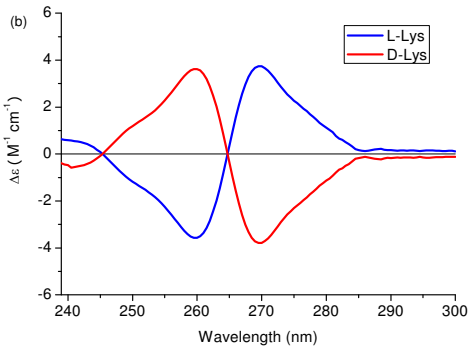
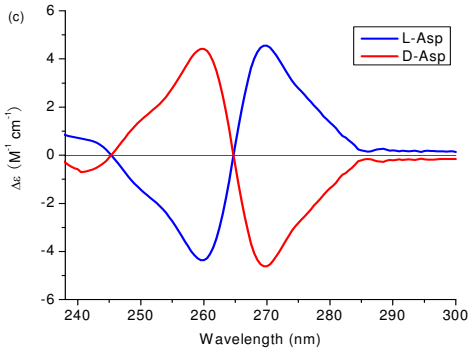
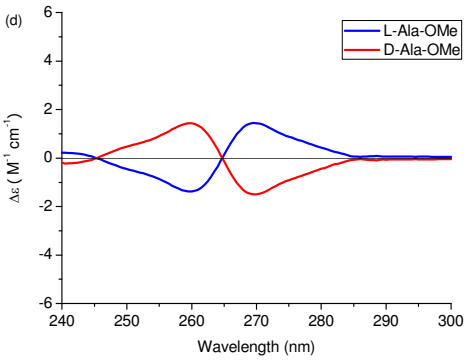
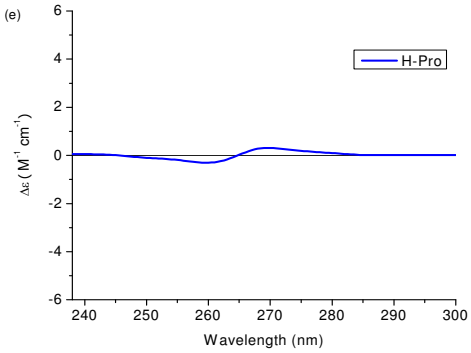
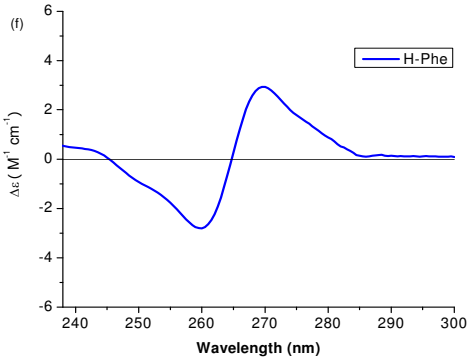

(a)
L-Val
D-Val
Δε(M-1 cm-1)
Wavelength (nm)

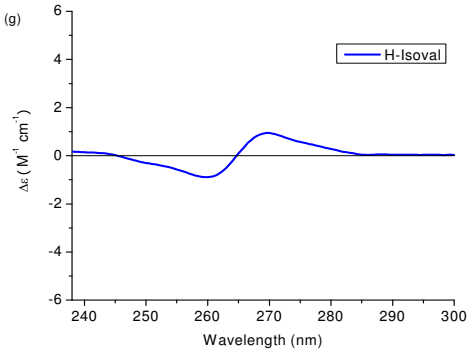

(b)
L-Lys
D-Lys
Δε (M-1 cm-1)
Wavelength (nm)

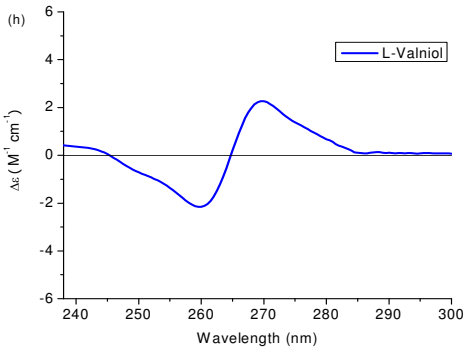

(c)
L-Asp
D-Asp
Δε (M-1 cm-1)
Wavelength (nm)


(d)
L-Ala-OMe
D-Ala-OMe
Δε (M-1 cm-1)
Wavelength (nm)


(e)
H-Pro
Δε (M-1 cm-1)
Wavelength (nm)


(f)
H-Phe
Δε (M-1 cm-1)
Wavelength (nm)


(g)
H-Isoval
Δε (M-1 cm-1)
Wavelength (nm)


(h)
L-Valniol
Δε (M-1 cm-1)
Wavelength (nm)

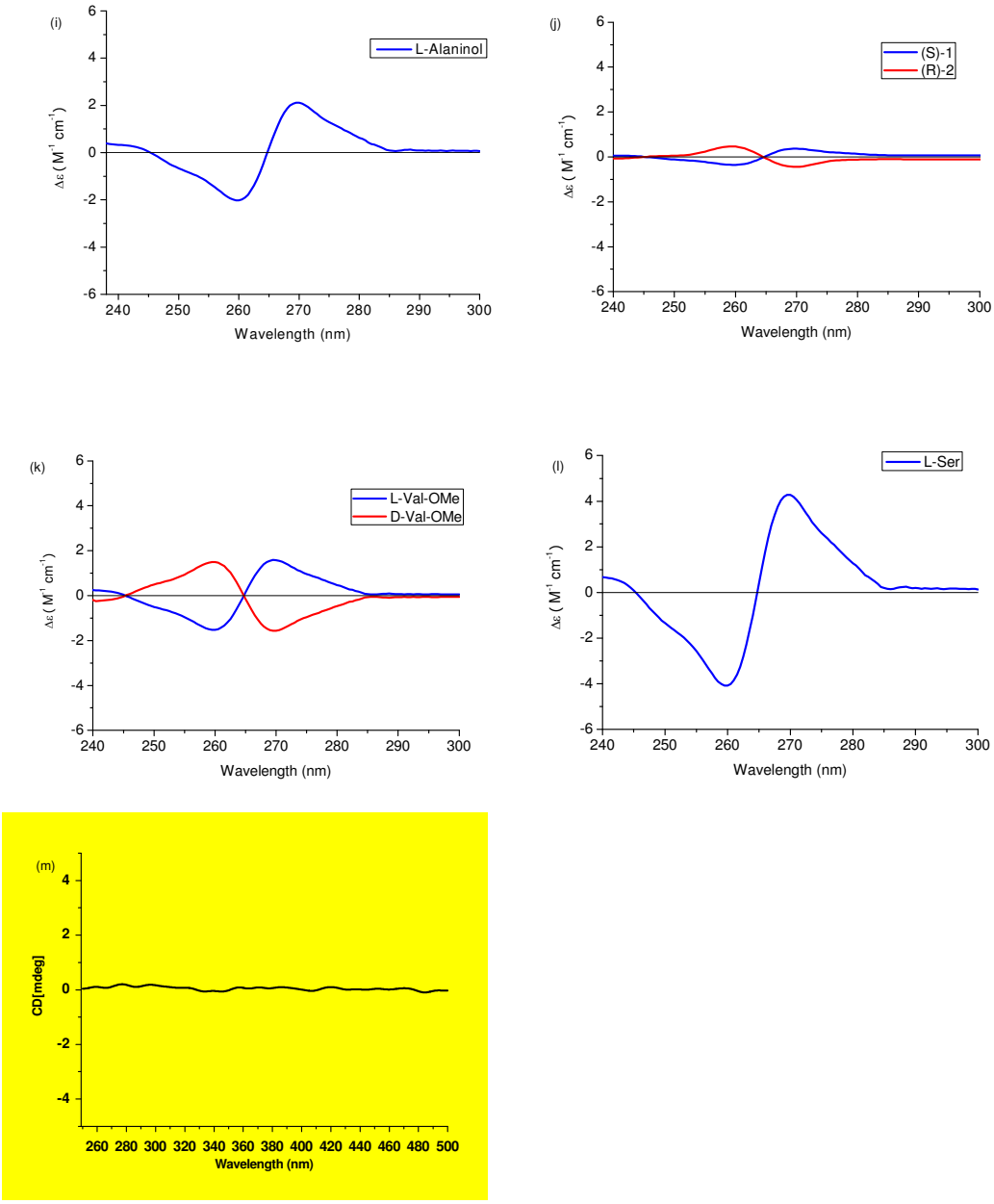


Figure S1. CD spectra of polymer **7a** in the presence of (a) Val, (b) Lys, (c) Asp, (d) Ala-OMe, (e) L-Pro, (f) L-Phe, (g) L-Isoval, (h) L-Valniol, (i) L-Alaniol, (j) (S)-1 and, (R)-2, (k) Val-OMe, and (l) L-Ser ([**7a**] = 2 mg/mL), and (m) without protonated amino acid..

Circular dichroism titration experiment. The CD titration experiments were carried out using D-Ala·$HClO_4$ to investigate the binding ability between polymer **7a** and protonated D-alanine. Stock solutions of **7a** (4 mg/mL, 8.2 mM, 20 mL) in CF_3CH_2OH and D-Ala·$HClO_4$ (19.4 mg/mL, 0.1 M, 5 mL) in CF_3CH_2OH were

prepared. To a flask was added the stock solution of **7a** (1 mL) and corresponding ratios of stock solutions of D-Ala and the resulting solutions were diluted with CF_3CH_2OH to make the total volume of the solution 2 mL. Titration CD spectra are shown in Figure S2. Plots of the CD intensities of the second Cotton ($\Delta\varepsilon_{2nd}$) of **7a** as a function of concentrations of D-Ala·$HClO_4$ gave a saturation binding isotherm (Figure 2). The Hill plot analysis of the data resulted in the binding constants of 6.6×10^2 M^{-1} and 6.4×10^2 M^{-1} for D-Ala and D-Val, respectively, according to the Hill equation, Log(i/(1-i))=nlog[L]+nlogK,where i = $\Delta\varepsilon_{2nd}(1:x)/\Delta\varepsilon_{2nd}(1:1)$, and 1:x is the molar ratio of **7a**:D-Ala·$HClO_4$, [L] is the concentration of D-Ala·$HClO_4$, and n is the Hill coefficient (Figure S2).

The titration with D-Val·$HClO_4$ was carried out in a similar manner.

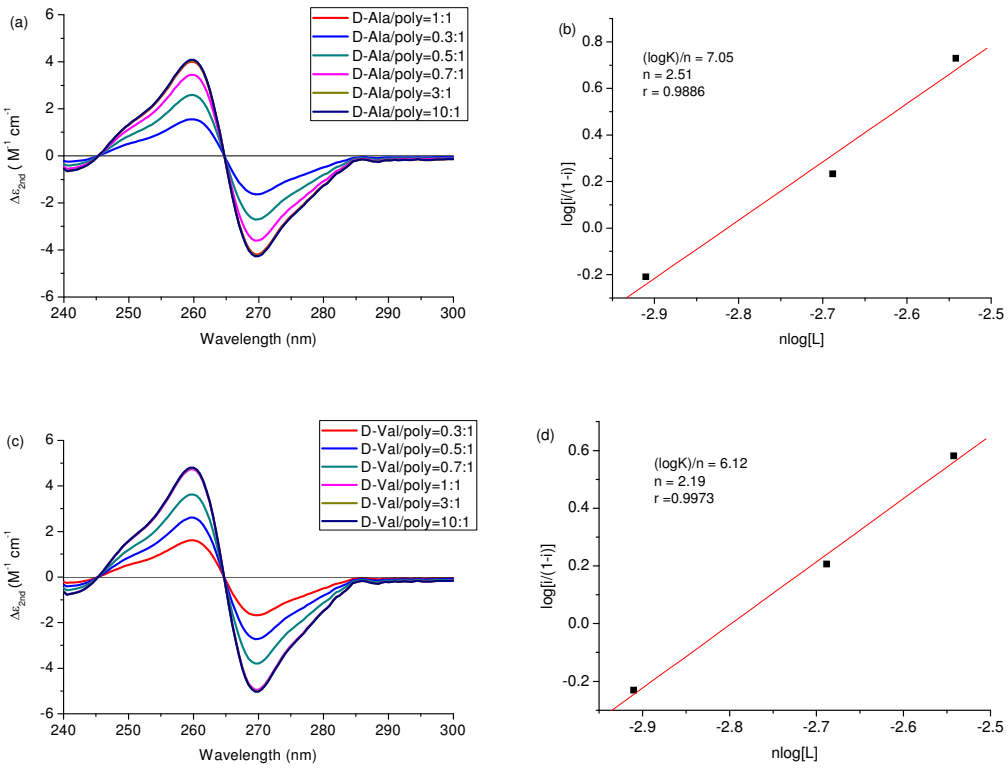


Figure S2. (a)CD curves of **7a** with different molar ratios of D-Ala·$HClO_4$ in CF_3CH_2OH at 20 °C, (b) Hill plot analysis of D-Ala·$HClO_4$ and **7a** complexes. (c) CD curves of **7a** with different molar ratios of D-Val·$HClO_4$ in CF_3CH_2OH at 20 °C (d) Hill plot analysis of D-Val·$HClO_4$ and **7a** complexes. ([**7a**] = 2 mg/mL).

Effect on enantiomeric excessof L-Val·$HClO_4$ on the CD curves of 7a. Stock

solutions of **7a** in CH_2Cl_2 (2 mg/mL, 4.1 mM, 100 mL), L-Val (9.6 mg/mL, 82 mM, 100 mL) in aqueous $HClO_4$ (0.1 M) D-Val (9.6 mg/mL (82 mM), 100 mL) in aqueous $HClO_4$ (0.1 M) were prepared. Aliquots of the solutions of L- and D-Val were added into six 10 mL volumetric flasks so that the % ee of Val (L- or D- rich) was adjusted to be 80, 60, 40, 20, 10, 5. To a flask were mixed the above valine mixture (5 mL) and and **7a** stock solution (5 mL) and the resulting mixture was thoroughly stirred for 18 h then stand for 8 h and the organic phase was separated for CD measurements. The experiments with a mixture of D- and L-Ala·$HClO_4$ were carried out in a similar manner.

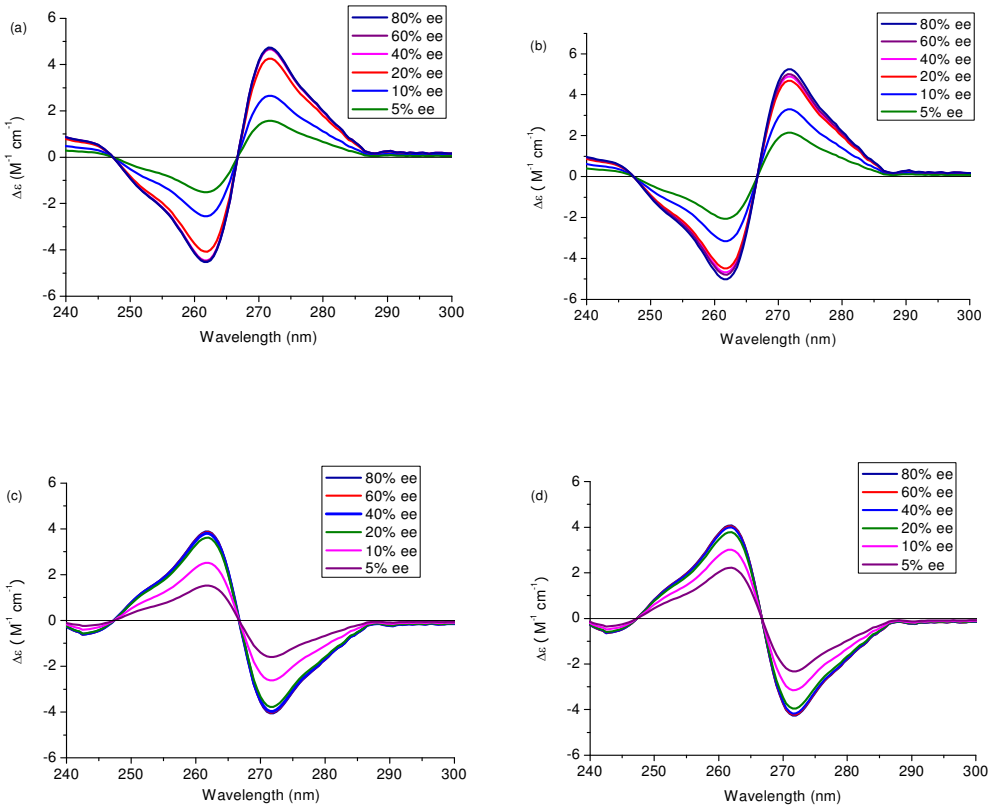


Figure S3. CD spectra of **7a** in the presence of different %ee of (a) L-Val at 20 °C, (b) L-Val at -10 °C, (c) D-Ala at 20 °C, and (d) D-Ala at -10 °C. [**7a**] = 2 mg/mL in CH_2Cl_2.

Effect on molar ratios of D-Ala-$HClO_4$ and glycine-$HClO_4$ on the CD curves of 7a. Stock solutions of **7a** in CH_2Cl_2 (2 mg/mL, 4.1 mM, 80 mL), D-Ala (7.3 mg/mL,

82 mM, 100 mL) in aqueous $HClO_4$ (0.1 M) and Gly (6.2 mg/mL, 82 mM, 100 mL) in aqueous $HClO_4$ (0.1 M) were prepared. Aliquots of the solutions of D-Ala and Gly were added into ten 10 mL volumetric flasks so that the molar percentages of D-Ala were adjusted to be 90, 80, 70, 60, 50, 40, 30, 20, 10, and 5. To a flask were mixed the above D-Ala and Gly mixture (5 mL) and **7a** stock solution (5 mL) and the resulting mixture was thoroughly stirred for 18 h then stand for 8 h and the organic phase was separated for CD measurements.

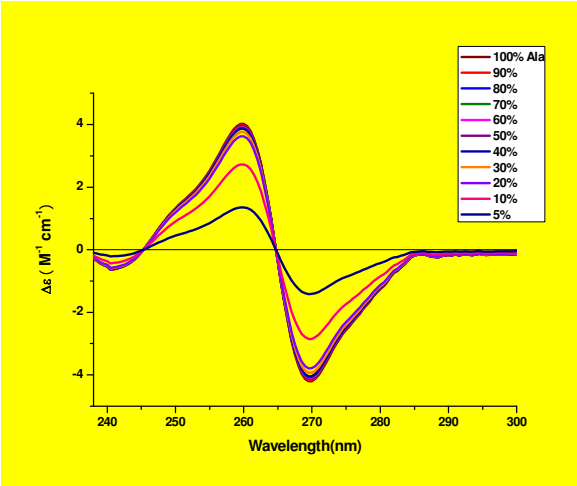


Figure S4. CD spectra of **7a** in the presence of different molar ratios of protonated D-alanine and glycine. [**7a**] = 2 mg/mL in CH_2Cl_2.

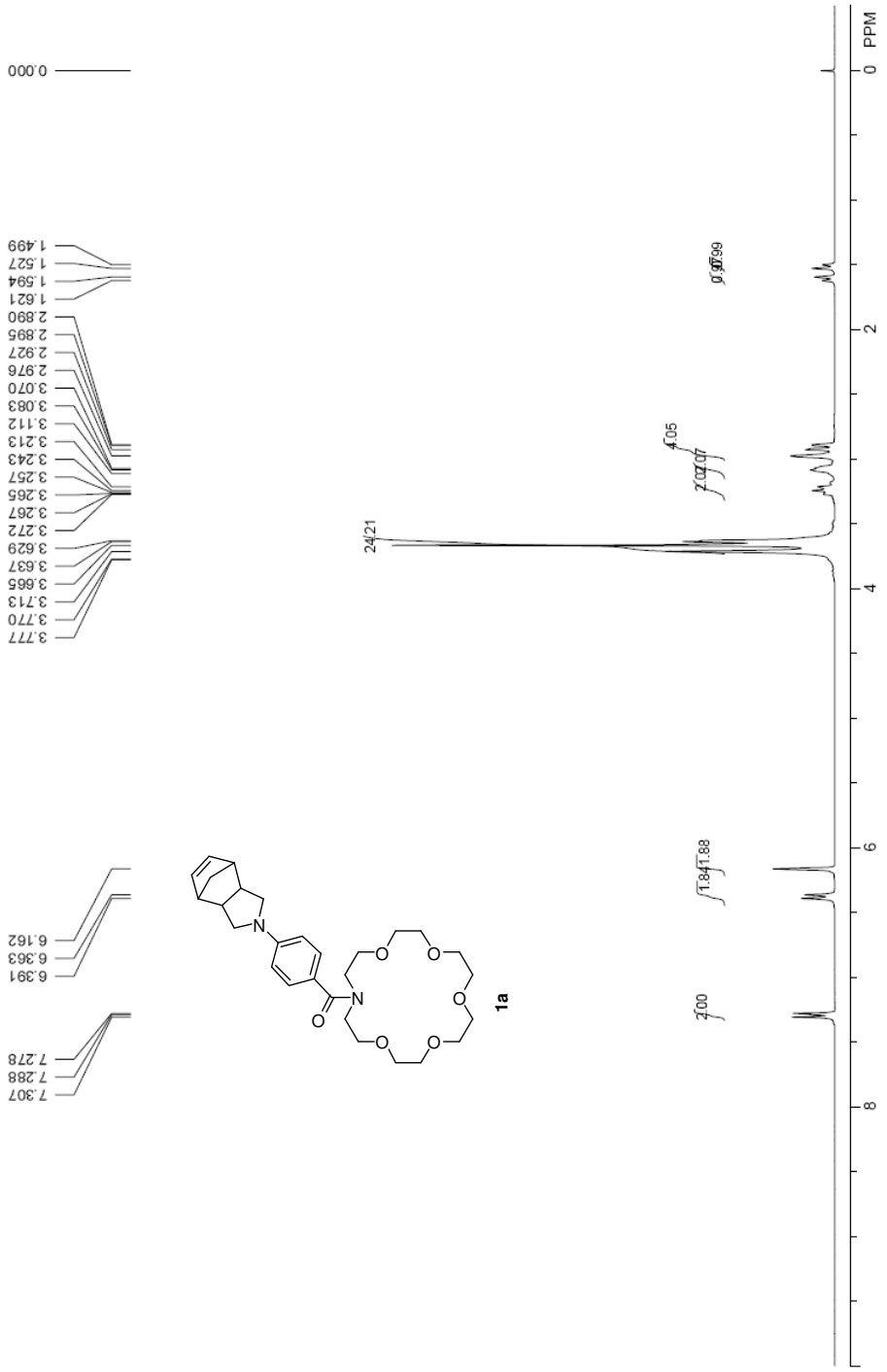


Figure S5. ^{1}H-NMR of **3a**

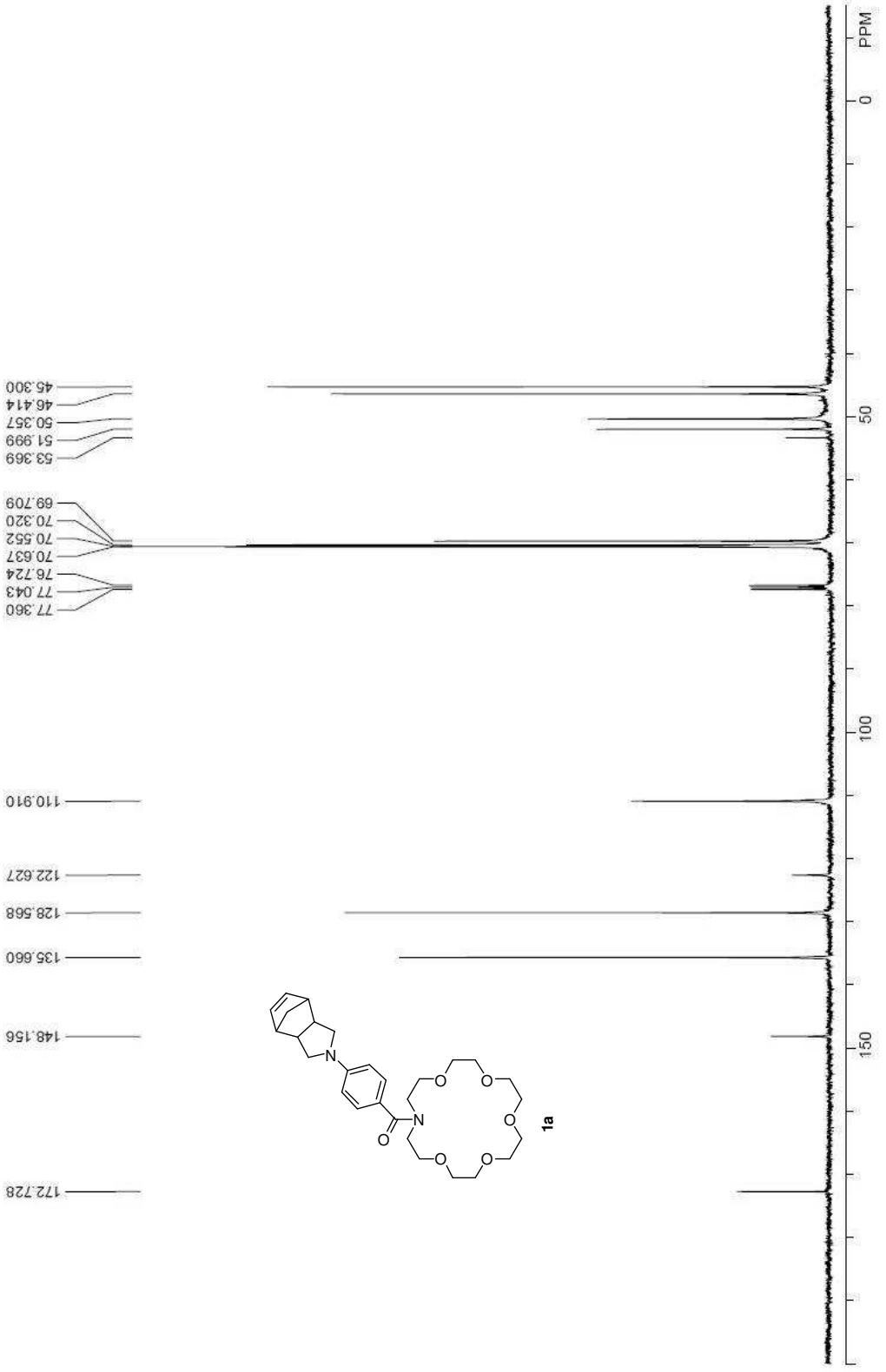


Figure S6. ^{13}C-NMR of **3a**

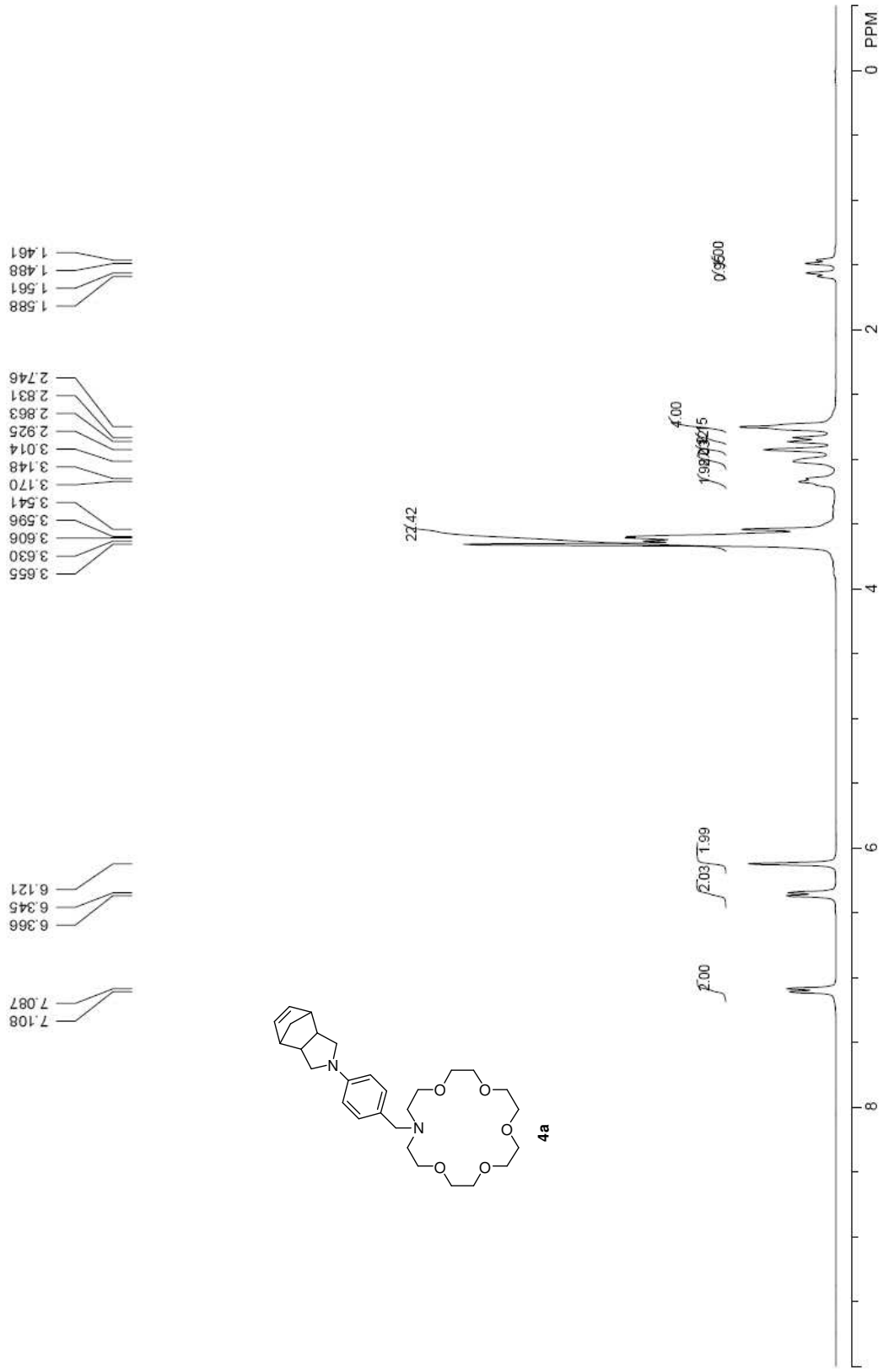


Figure S7. ^{1}H-NMR of **6a**

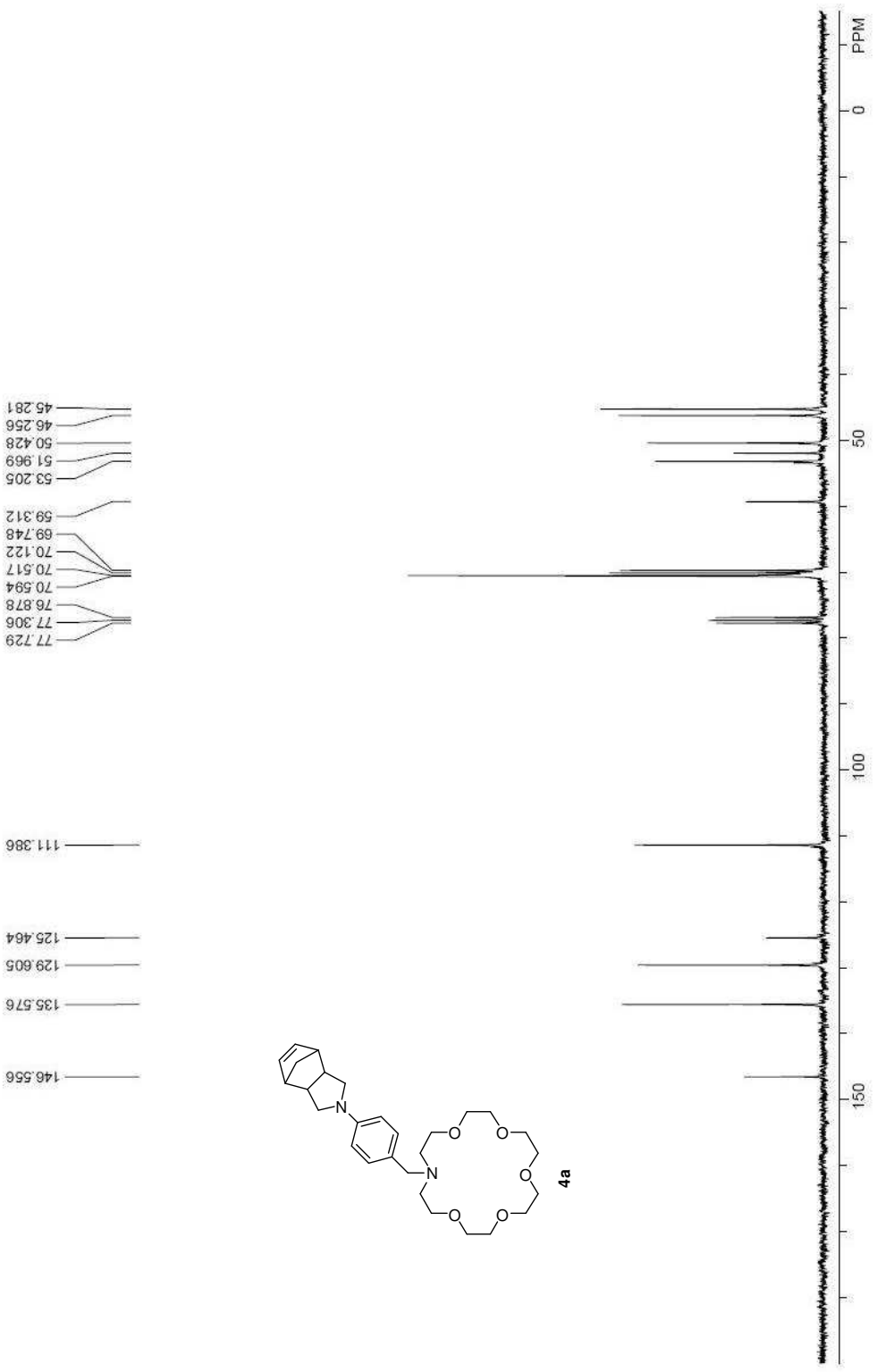


Figure S8. ^{13}C-NMR of **6a**

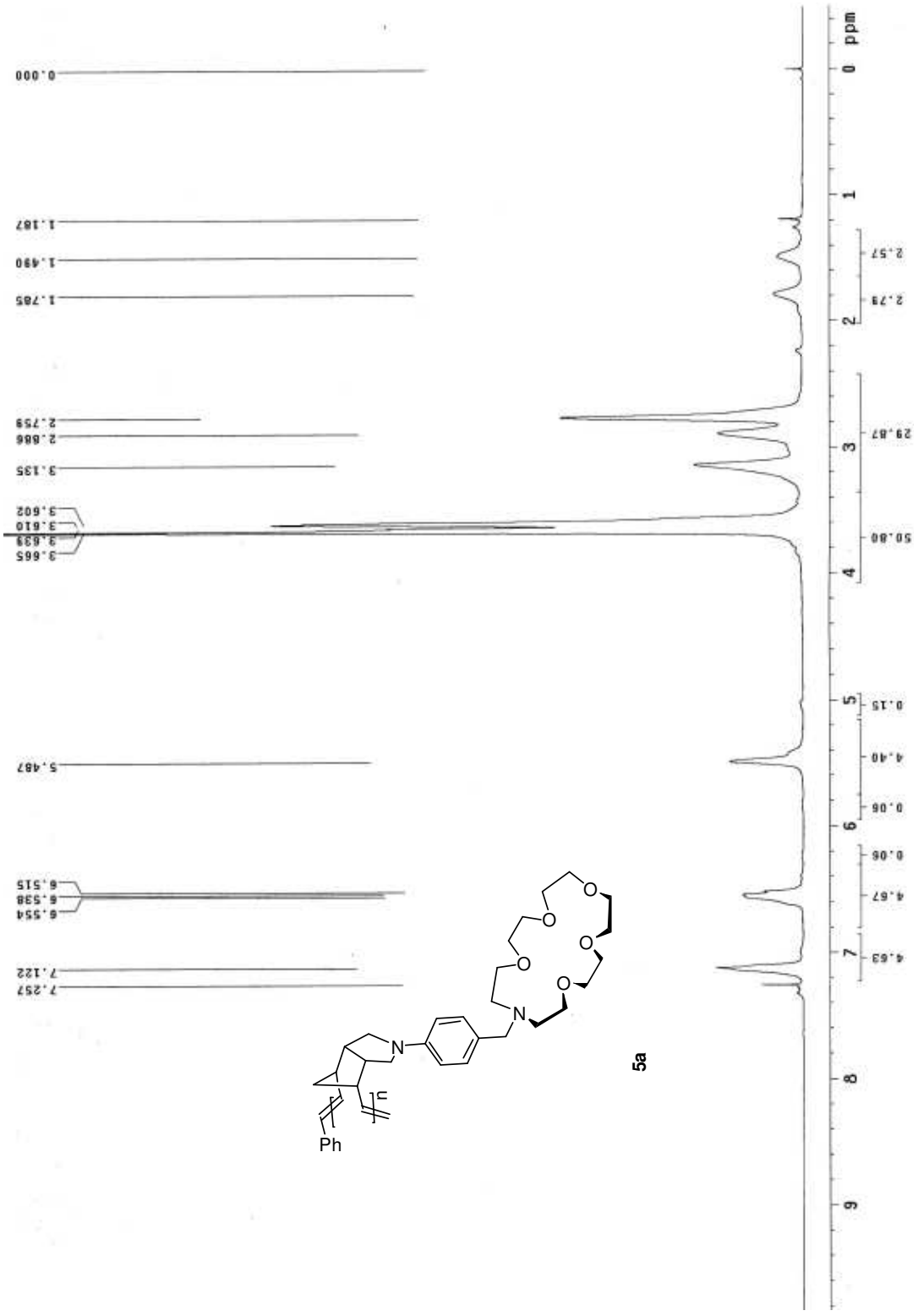


Figure S9. ^{1}H-NMR of **7a**

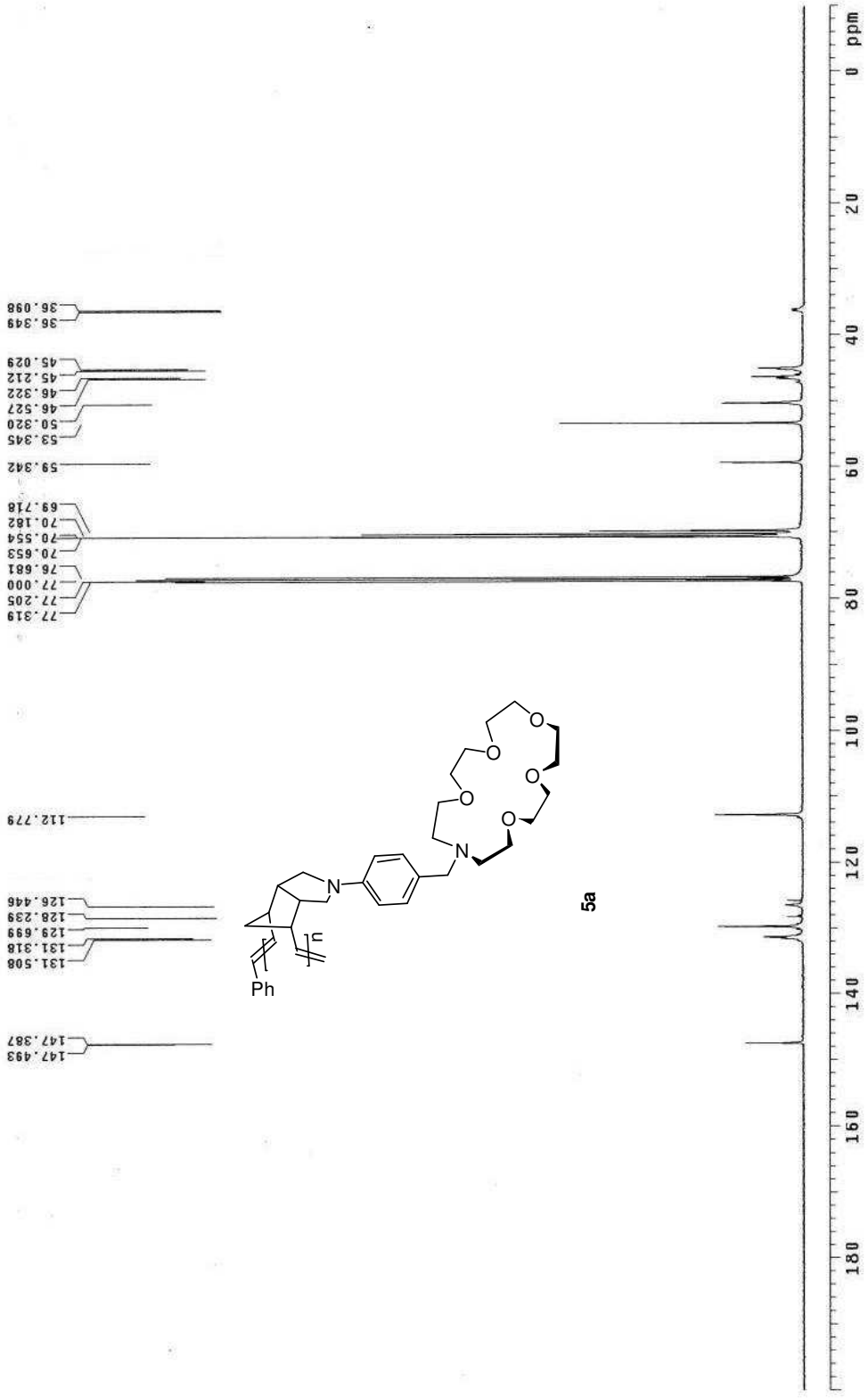


Figure S10. ^{13}C-NMR of **7a**

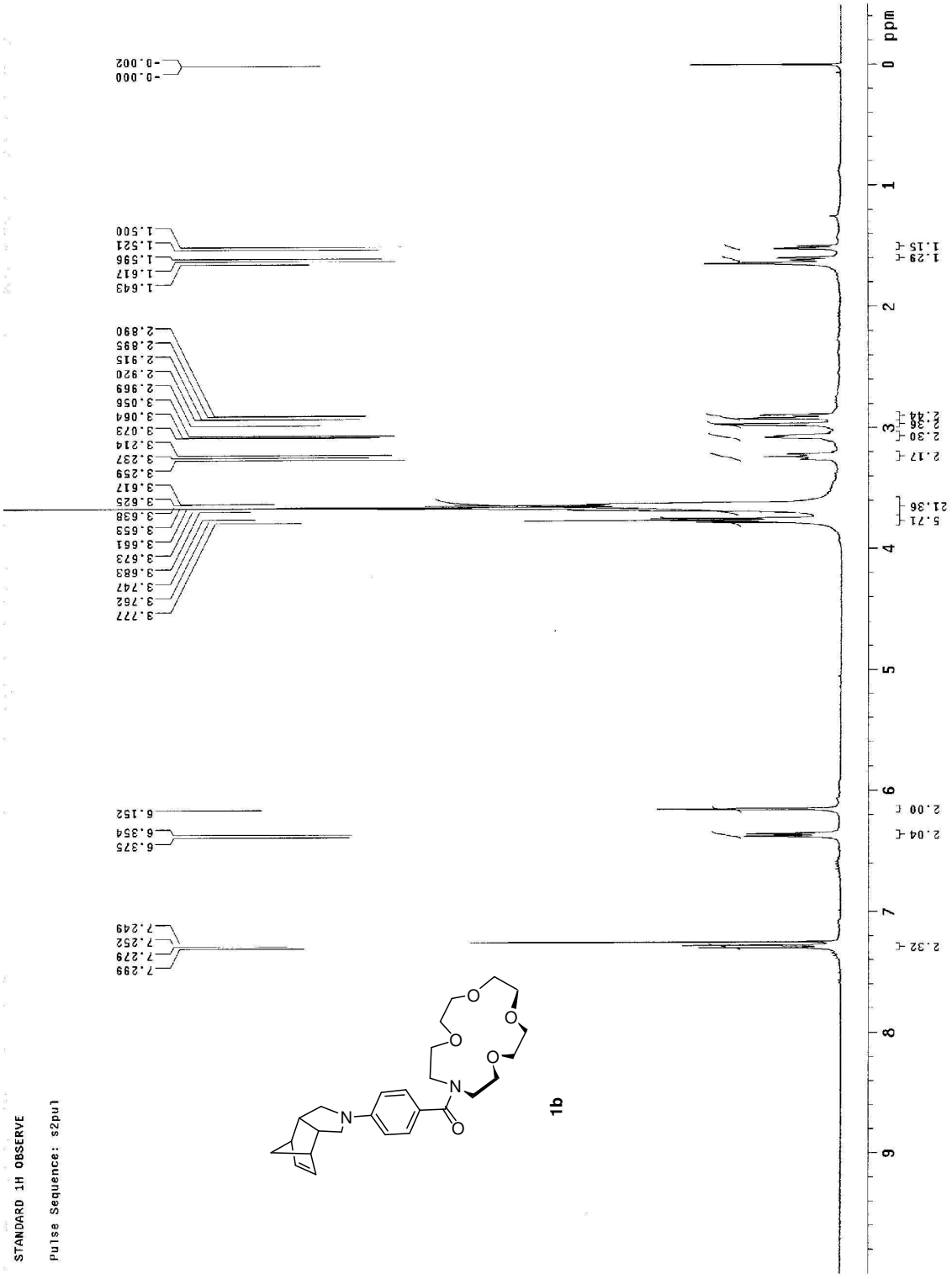


Figure S11. ^{1}H-NMR of **3b**

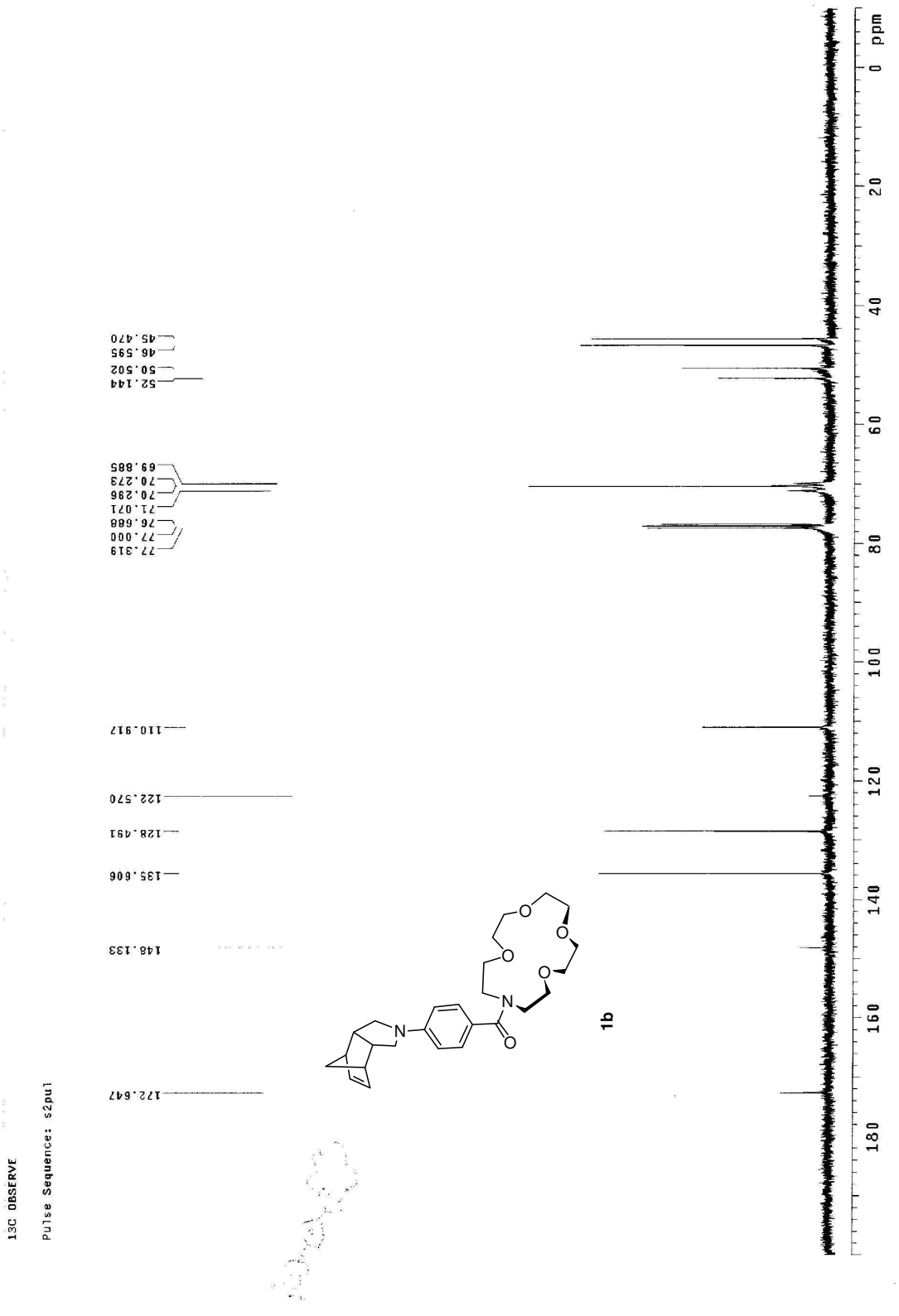


Figure S12. ^{13}C-NMR of **3b**

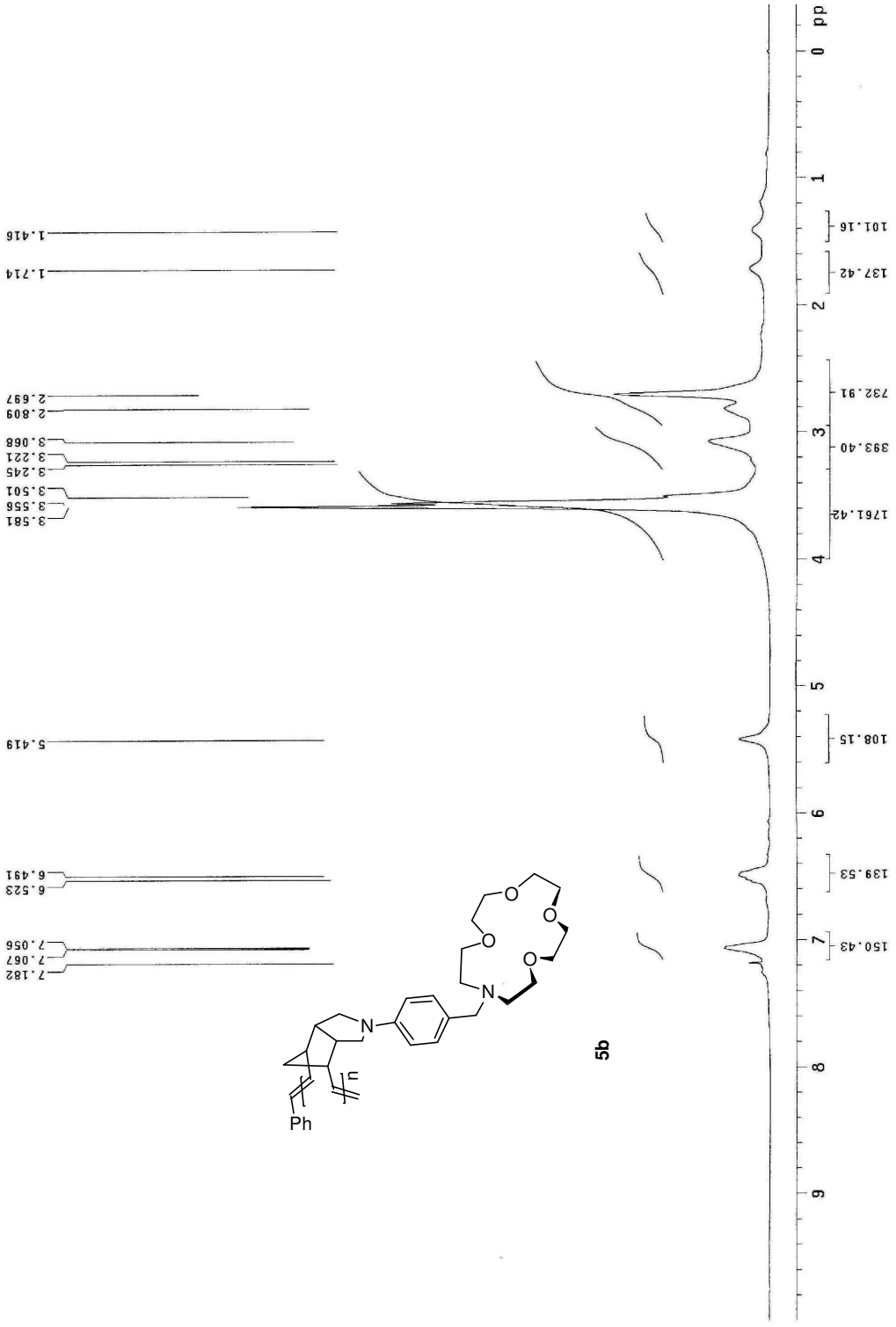


Figure S13. ^{1}H-NMR of **7b**

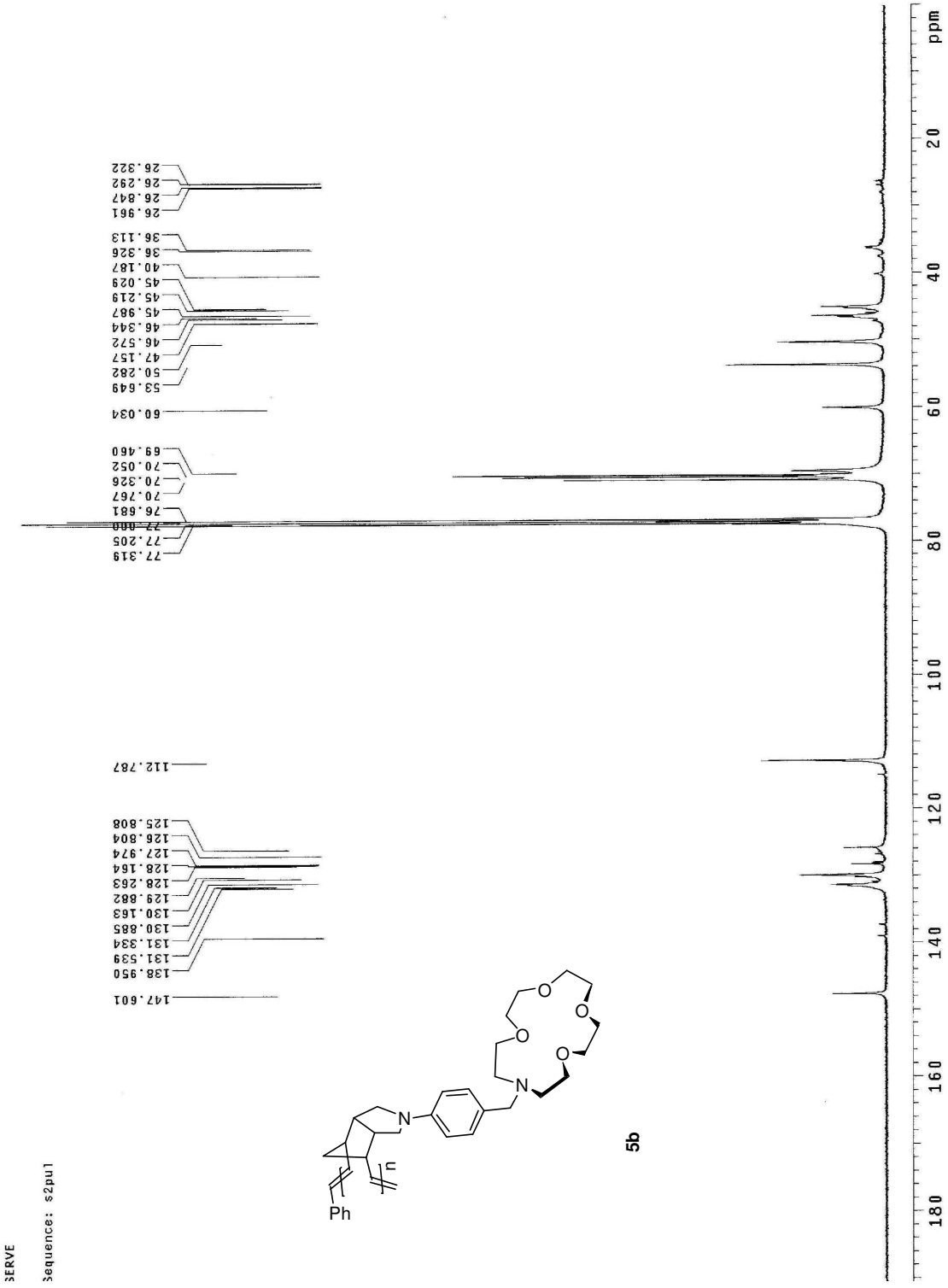


Figure S14. ^{13}C-NMR of **7b**

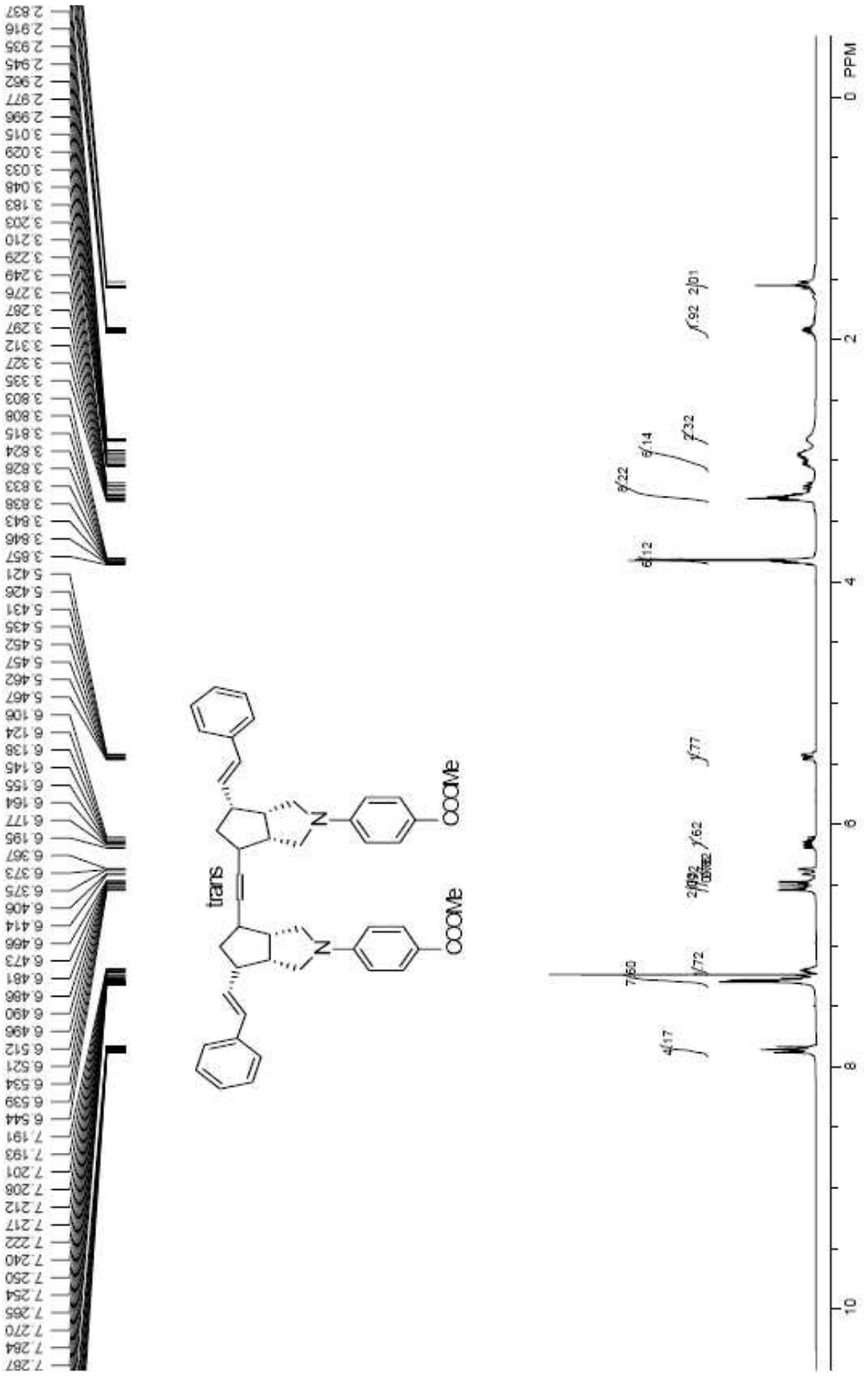


Figure S15. ^{1}H-NMR of **8**

Figure S16. ^{13}C-NMR of **8**

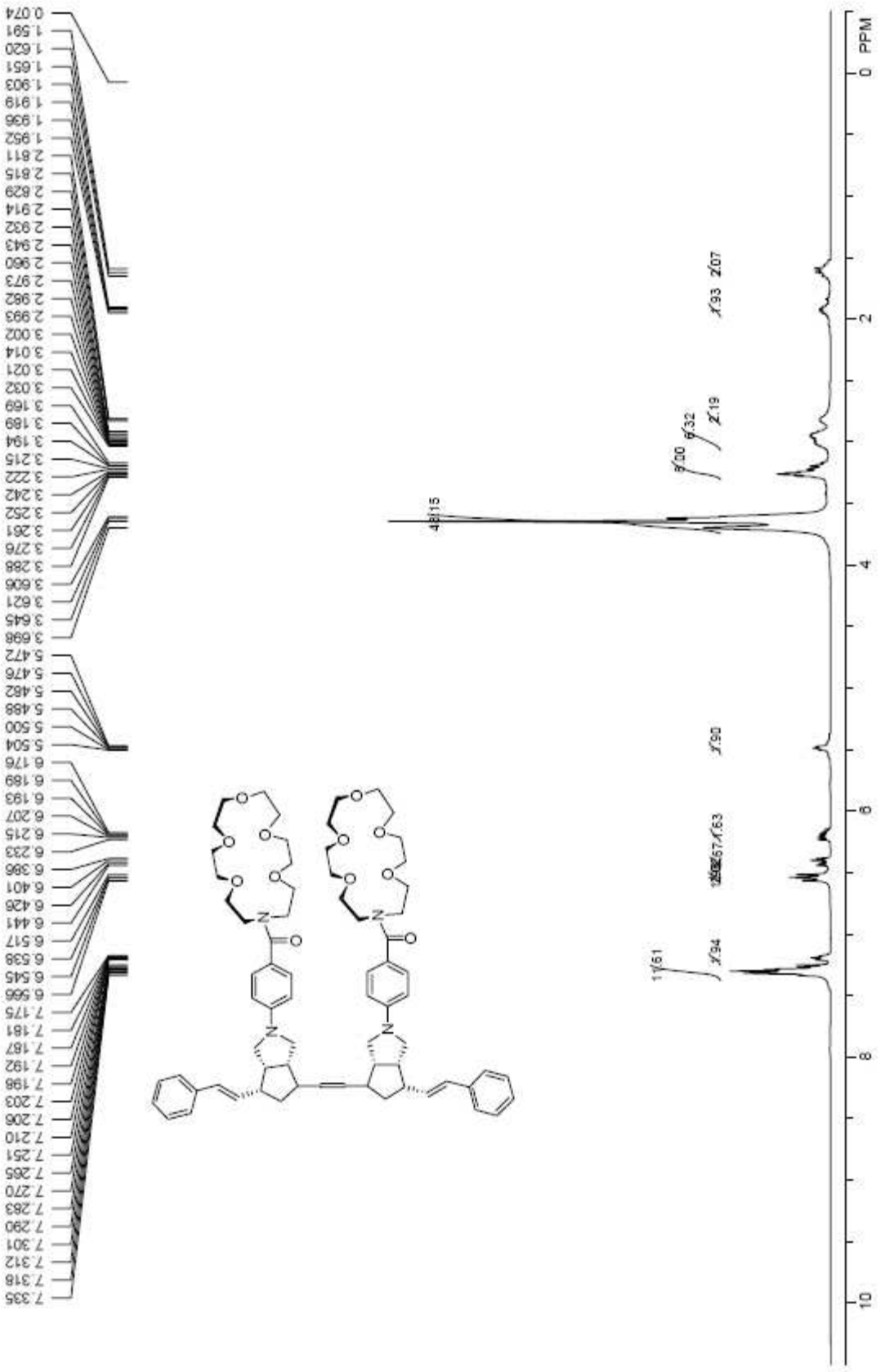


Figure S17. ^{1}H-NMR of **9**

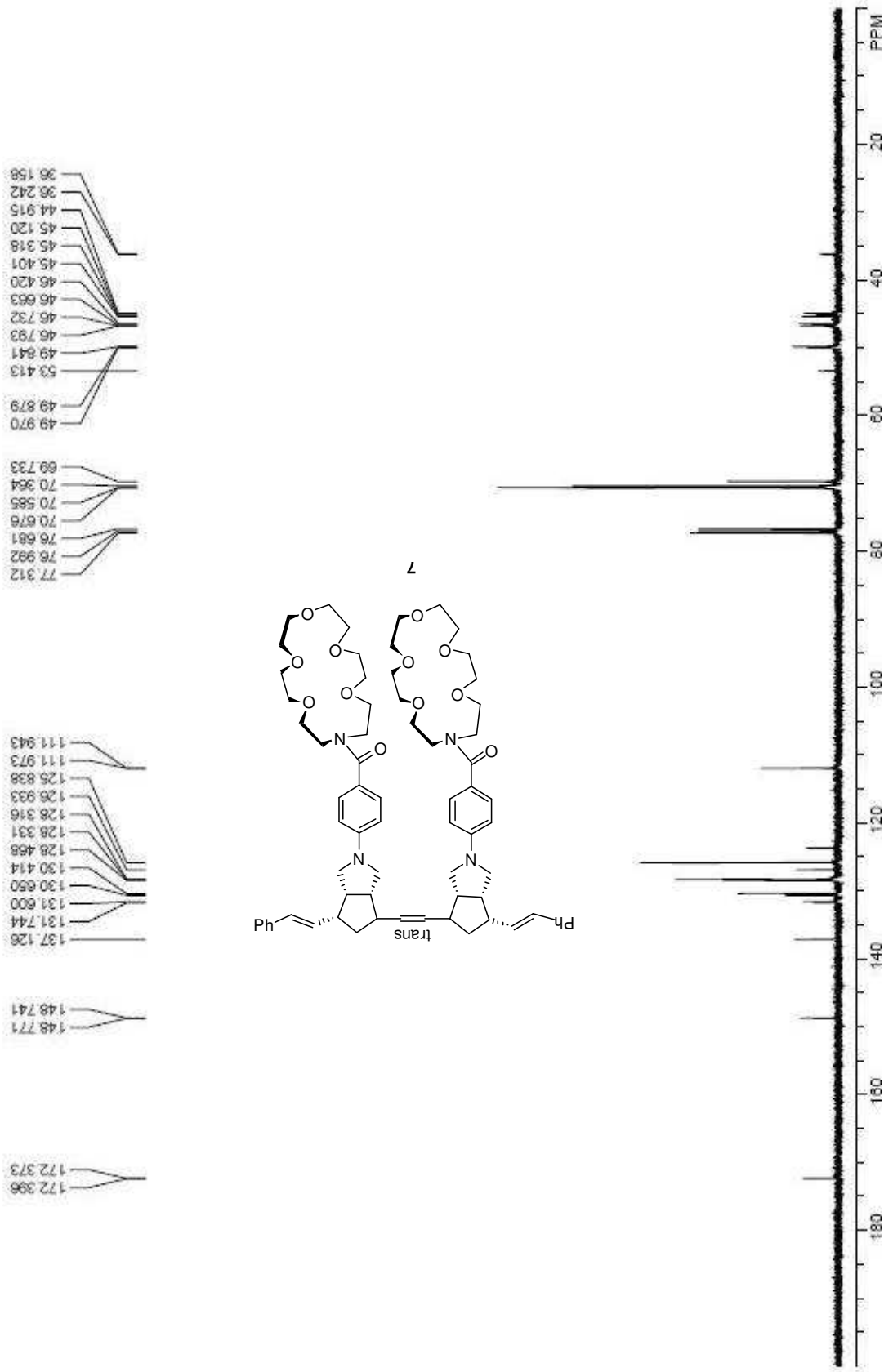


Figure S18. ^{13}C-NMR of **9**

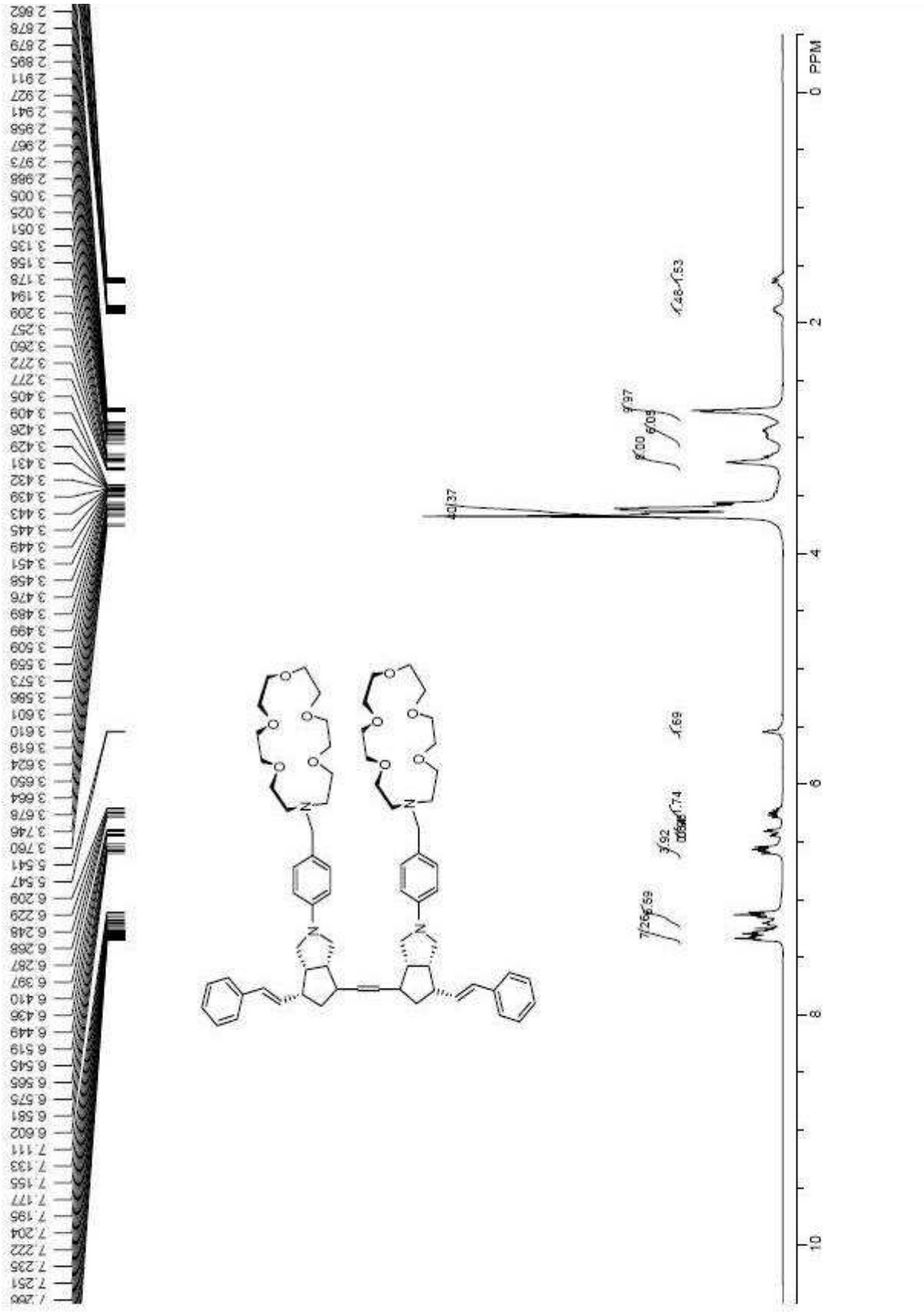


Figure S19. ^{1}H-NMR of **10**

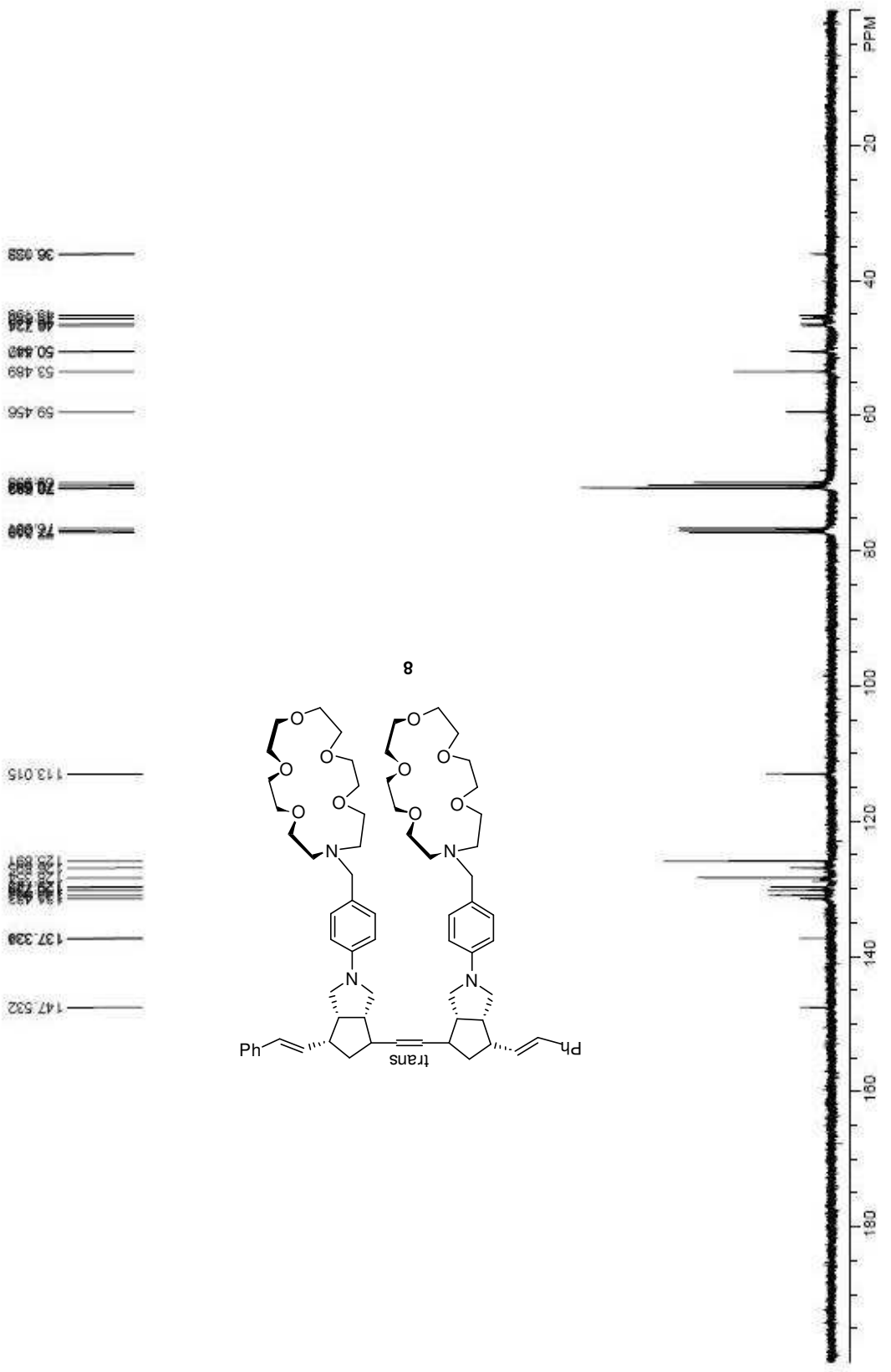
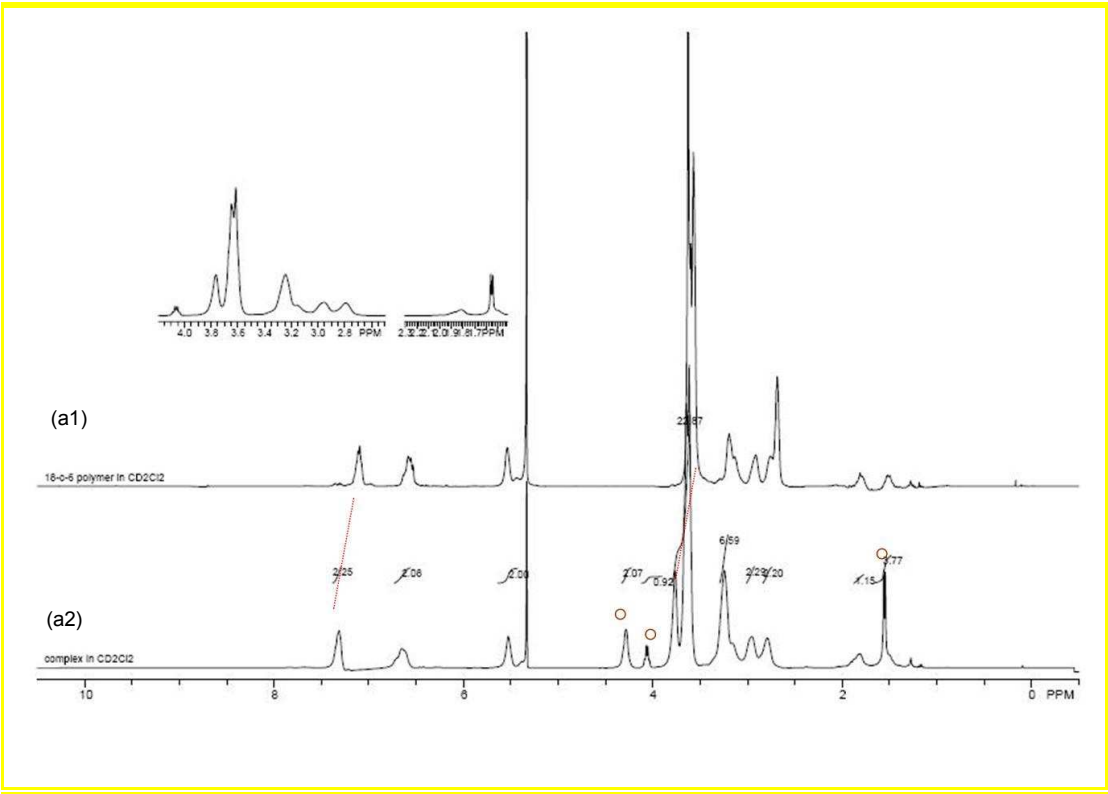


Figure S20. ^{13}C-NMR of **10**



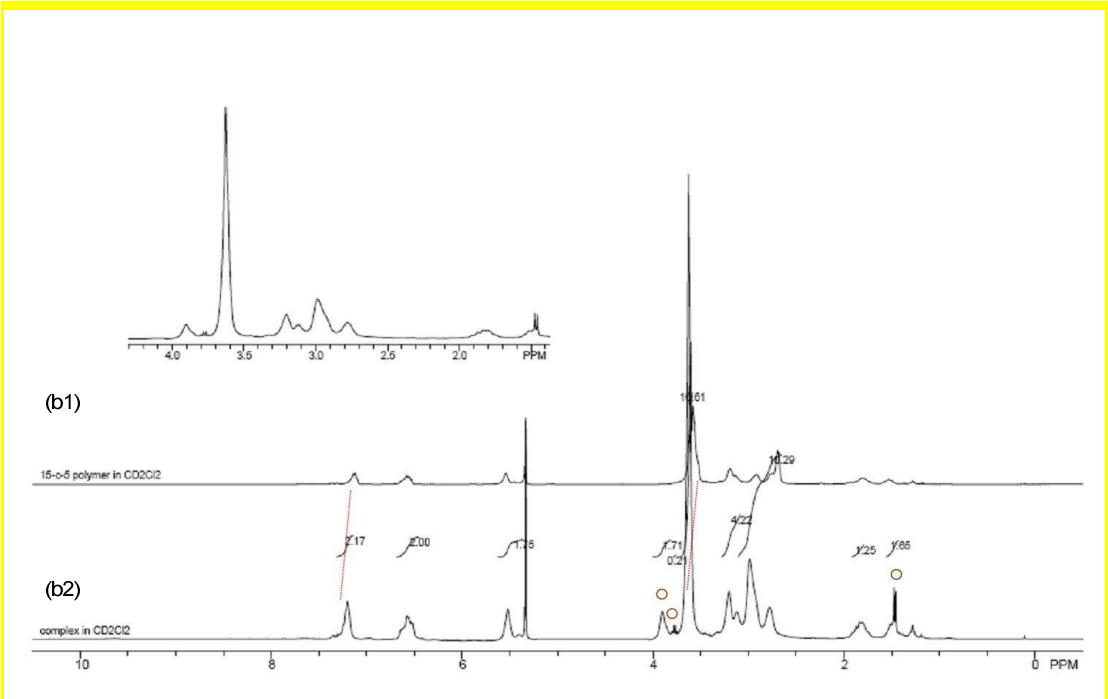


Figure S21. ^{1}H NMR spectra of (a1) **7a**, (b1) **7b**, the extraction of protonated D-alanine with (a2) **7a** and (b2) **7b** in CD_2Cl_2. The relative ratio of signals around d 1.5 and 7.3 was 3.77 in (a2) to 2 indicating approximate one to one complex would be formed. On the other hand, the relative ratio of signals around d 1.5 to 7.3 was 1.66 to 2 (b2) suggesting that less than 25% D-alanine was extracted to the organic phase.

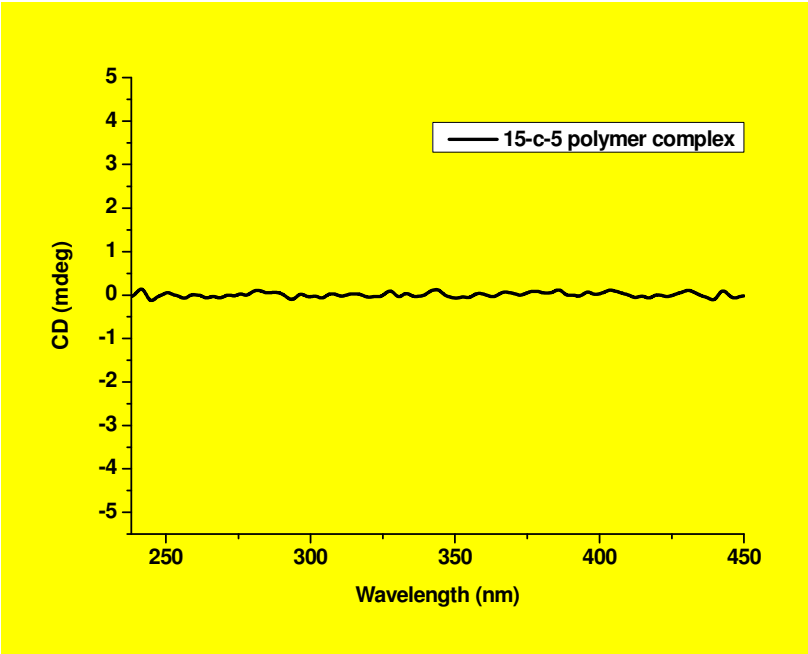


Figure S22. CD spectrum of CD_2Cl_2 solution of **7b** after extraction experiment with protonated D-alanine.