Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Complexes of amino acids with a crown-ether derivative of 4-styrylpyridine. Monotopic or ditopic?

O. A. Fedorova,*[a], Yu. V. Fedorov,[a] I. E. Labazava,[a] E. N. Gulakova,[a] J. Saltiel*[b]

Electronic Supplementary Information

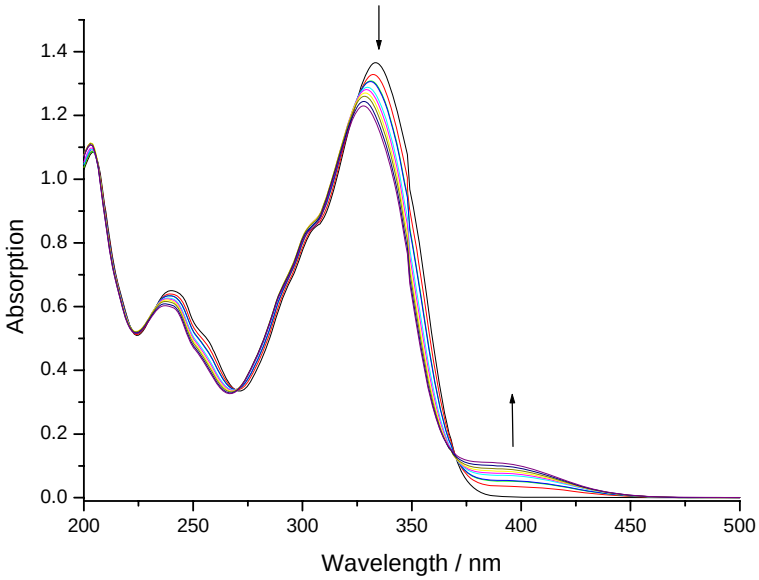

Fig. S1. UV-Vis spectra of ligand *E*-**1** alone and in the presence of protonated amino acid **A2** in MeCN. [*E*-**1**] = 5 x 10^{-5} M to 4.73 x 10^{-5} M, [**A2**] = 0 to 4 x 10^{-4} M. The shoulder at 390 nm is due to protonation by < 0.5% excess $HClO_4$ in **A2**.

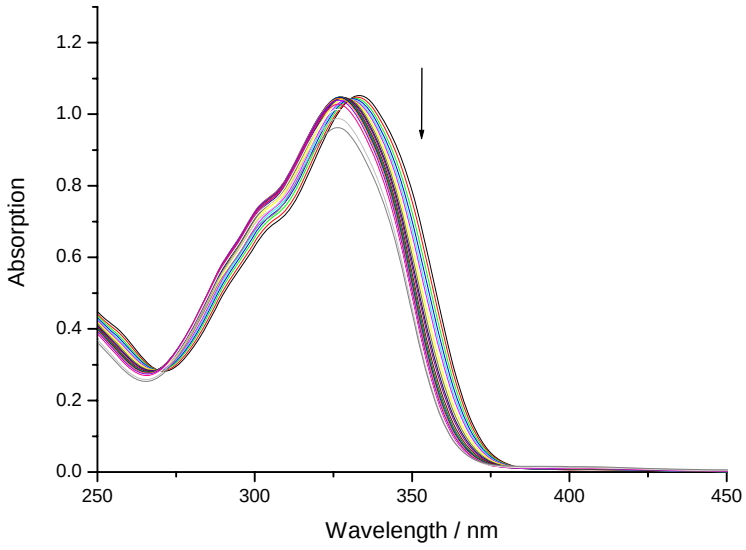

Fig. S2. UV-Vis spectra of ligand *E*-**1** alone and in the presence of protonated amino acid **A5** in CH_3CN, 25 °C. [*E*-**1**] = 4.0 x 10^{-5} – 3.53 x 10^{-5} M, [**A5**] = 0 – 2.3 x 10^{-3} M.

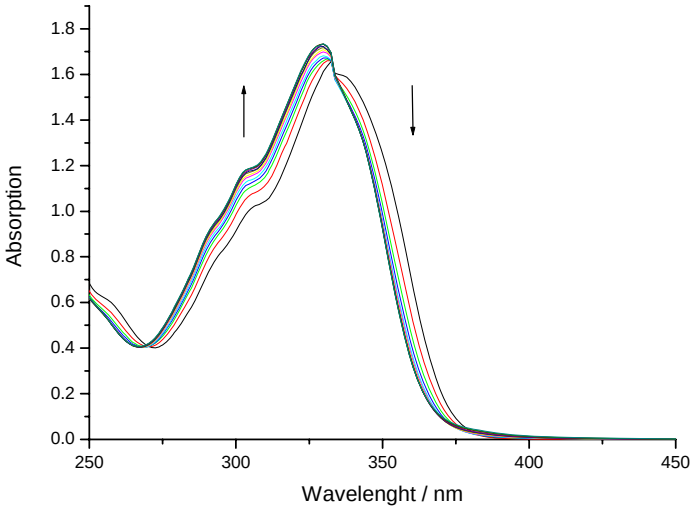

Fig. S3. UV-Vis spectra of ligand *E*-**1** alone and in the presence of protonated amino acid **A10** in CH_3CN, 25 °C. [*E*-**1**] = 6.1 x 10^{-5} – 5.9 x 10^{-5} M, [**A10**] = 0 – 5.9 x 10^{-4} M.

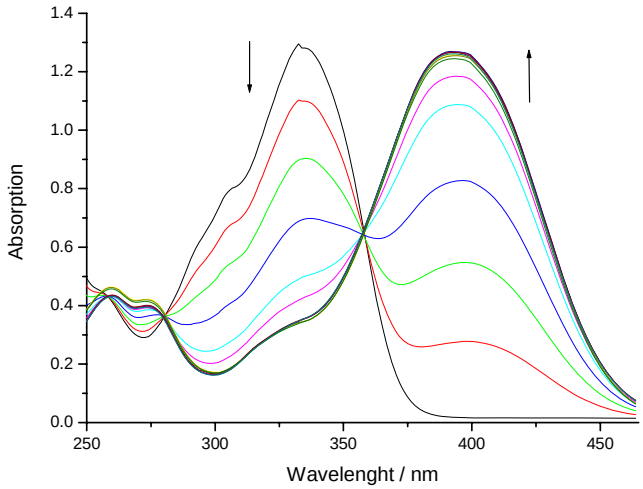

Fig. S4. UV-Vis spectra of ligand *E*-**1** alone and in the presence of $HClO_4$ in CH_3CN, 25 °C. [*E*-**1**] = 4.9 x 10^{-5} – 4.7 x 10^{-5} M, [$HClO_4$] = 0 – 6.85 x 10^{-5} M.

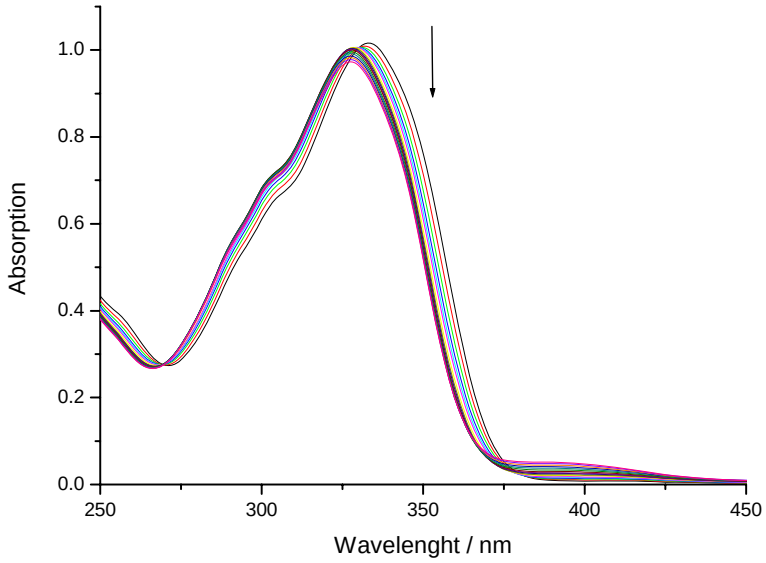

Fig. S5. UV-Vis spectra of ligand *E*-**1** alone and in the presence of NH_4ClO_4 in CH_3CN, 25 °C. [*E*-**1**] = 3.9 x 10^{-5} – 3.8 x 10^{-5} M, [NH_4ClO_4] = 0 – 6.1 x 10^{-4} M.

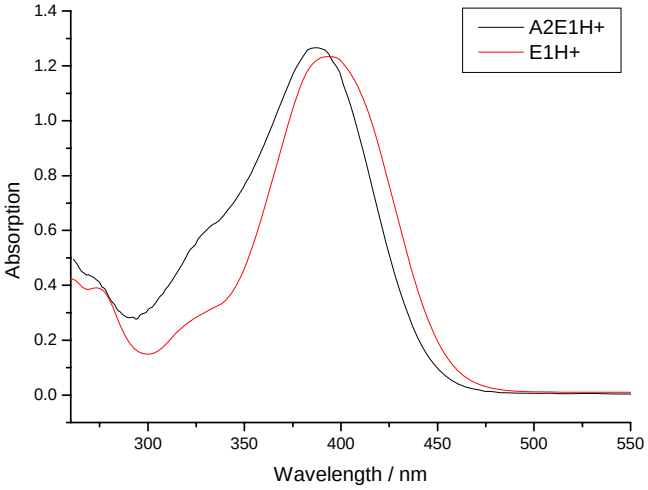

Fig. S6. Comparison of the *E*-**1•H**$^+$ and ***E***-1•**H**$^+$**•A2** spectra in Figs. 1 and 3, respectively.

^{1}H NMR characterization:

E-4-[2-(6,7,9,10,12,13,15,16,18,19-Decahydro-5,8,11,14,17,20-hexaoxa-benzocyclo-octadecen-2-yl)-vinyl]-pyridine (*E*-**1**): ^{1}H NMR (500.13 MHz, CD_3CN): δ = 3.53 (m, 4H, 2 OCH_2); 3.56 (m, 4H, 2 OCH_2); 3.62 (m, 4H, 2 OCH_2); 3.76 and 3.78 (both m, 4H, 2 OCH_2); 4.11 and 4.16 (both m, 4H, 2 OCH_2); 6.96 (d, 1H, H-5′, *J* = 8.2 Hz); 7.14 (d, 1H, H-b, *J* = 16.3 Hz); 7.15 (dd, 1H, H-6′, *J* = 1.4, 8.2 Hz); 7.31 (d, 1H, H-2′, *J* = 1.4 Hz); 7.46 (d, 1H, H-a, *J* = 16.3 Hz,); 7.51 (d, 2H, H-3, H-5, *J* = 5.9 Hz); 8.52 (d, 2H, H-2, H-6, *J* = 5.9 Hz).

E-**1**·$HClO_4$:^{1}H NMR (500.13 MHz, CD_3CN): δ = 3.55 (m, 4H, 2 OCH_2); 3.59 (m, 4 H, 2 OCH_2); 3.66 (m, 4H, 2 OCH_2); 3.86 (m, 4H, 2 OCH_2); 4.02 and 4.13 (both m, 4H, 2 OCH_2); 6.86 (d, 1H, H-5′, *J* = 8.5 Hz); 6.86 (d, 1H, H-b, *J* = 16.5 Hz); 6.99 (s, 1H, H-2′); 7.15 (d, 1H, H-6′, *J* = 8.5 Hz); 7.37 (d, 1H, H-a, *J* = 16.5 Hz,); 7.56 (d, 2H, H-3, H-5, *J* = 5.5 Hz); 8.60 (m, 2H, H-2, H-6, splitting by adjacent H-3(H-5) and pyridinium protons).

E-**1**·NH_4ClO_4: ^{1}H NMR (500.13 MHz, CD_3CN): δ = 3.60 (m, 4H, 2 OCH_2); 3.64 (m, 8H, 4 OCH_2); 3.83 (m, 4H, 2 OCH_2); 4.20 (m, 4H, 2 OCH_2); 6.96 (d, 1H, H-5′, *J* = 8.5 Hz); 7.05 (d, 1H, H-b, *J* = 16.5 Hz); 7.15 (d, 1H, H-6′, *J* = 8.6 Hz); 7.21 (s, 1H, H-2′); 7.40 (d, 1H, H-a, *J* = 16.5 Hz); 7.47 (d, 2H, H-3, H-5, *J* = 4.9 Hz); 8.53 (broad s, 2H, H-2, H-6, broadened by adjacent H-3(H-5) and proton).

E-**1**·**A2**: ^{1}H NMR (500.13 MHz, CD_3CN): δ = 2.00 - 2.40 (m, 4H, CH_2N, CH_2CO_2H); 3.71 (m, 4H, 2 OCH_2); 3.73 (m, 4H, 4 OCH_2); 3.77 (m, 4H, 2 OCH_2); 3.85 and 3.89 (both m, 4H, 2 OCH_2); 4.04 and 4.17 (both m, 4H, 2 OCH_2); 6.88 (m, 2H, H-5′, H-b, *J* = 16.4 Hz); 7.02 (s, 1H, H-2′); 7.15 (d, 1H, H-6′, *J* = 8.5 Hz); 7.37 (d, 1H, H-a, *J* = 16.4 Hz,); 7.52 (d, 2H, H-3, H-5, *J* = 6.7 Hz); 8.53 (d, 2H, H-2, H-6, *J* = 6.7 Hz).

E-**1**·$\mathbf{H^+}$·**A2:** ^{1}H NMR (500.13 MHz, CD_3CN): δ = 2.00 - 2.40 (m, 4H, CH_2N, CH_2CO_2H); 3.71 (m, 4H, 2 OCH_2); 3.77 (m, 8H, 4 OCH_2); 3.85 and 3.88 (both m, 4H, 2 OCH_2); 4.05 and 4.15 (both m, 4H, 2 OCH_2); 6.89 (d, 1H, H-5′, *J* = 8.5 Hz); 6.87 (d, 1H, H-b, *J* = 16.4 Hz); 7.11 (s, 1H, H-2′); 7.17 (d, 1H, H-6′, *J* = 8.5 Hz); 7.44 (d, 1H, H-a, *J* = 16.4 Hz,); 7.52 (d, 2H, H-3, H-5, *J* = 6.7 Hz) ; 8.59 (d, 2H, H-2, H-6, *J* = 6.7 Hz).

E-**1**·**A5**: ^{1}H NMR (500.13 MHz, CD_3CN): δ = 1.27 (m, 2H, γ-CH_2 from **A5**); 1.48 (m, 4H, β- and δ-CH_2 from **A5**); 2.19 (t, 2H, CH_2COOH, *J* = 7.3 Hz); 2.83 (t, 2H, $CH_2NH_3^+$, *J* = 7.3 Hz); 3.67 (m, 4H, 2 OCH_2); 3.70 (m, 4H, 2 OCH_2); 3.74 (m, 4H, 2 OCH_2); 3.88 and 3.92 (both m, 4H, 2 OCH_2); 4.26 and 4.32 (both m, 4H, 2 OCH_2); 7.05 (d, 1H, H-5′, *J* = 8.5 Hz); 7.15 (d, 1H, H-b, *J* = 16.5 Hz); 7.22 (dd, 1H, H-6′, *J* = 1.8, 8.5 Hz); 7.31 (d, 1H, H-2′, *J* = 1.8 Hz); 7.41 (d, 1H, H-a, *J* = 16.5Hz,); 7.46 (d, 2H, H-3, H-5, *J* = 5.5 Hz); 8.55 (d, 2H, H-2, H-6 *J* = 5.5 Hz.

E-**1**·**A10**: ^{1}H NMR (500.13 MHz, CD_3CN): δ = 1.12 – 1.32 (m, 12H, $(CH_2)_6$); 1.45 (m, 2H, β-CH_2 from **A10**); 1.51 (m, 2H, ι-CH_2 from **A10**); 2.24 (t, 2H, CH_2COOH, *J* = 7.3 Hz); 2.83 (t, 2H, $CH_2NH_3^+$, *J* = 7.3 Hz); 3.68 (m, 4H, 2 OCH_2); 3.71 (m, 4H, 2 OCH_2); 3.75 (m, 4H, 2 OCH_2); 3.89 and 3.92 (both m, 4H, 2 OCH_2); 4.26 and 4.31 (both m, 4H, 2 OCH_2); 7.05 (d, 1H, H-5′, *J* = 8.6 Hz); 7.12 (d, 1H, H-b, *J* = 16.5 Hz); 7.23 (dd, 1H, H-6′, *J* = 1.8, 8.5 Hz); 7.32 (d, 1H, H-2′, *J* = 1.8 Hz); 7.41 (d, 1H, H-a, *J* = 16.5Hz,);

7.49 (broad s, 2H, H-3, H-5, broadening due to splitting by H-2(H-6)); 8.56 (very broad s, 2H, H-2, H-6, broadening due to splitting by H-3(H-5) and H bonding at N).

Z-4-[2-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-yl)vinyl]pyridine (*Z*-**1**): ^{1}H NMR (300.16 MHz, CD_3CN): δ = 3.56 (m, 4 H, 2 OCH_2); 3.58 (m, 6 H, 3 OCH_2); 3.61 and 3.75 (both m, 6 H, 3 OCH_2); 3.87 and 4.13 (both m, 4 H, 2 OCH_2); 6.51 (d, 1 H, H-b, *J* = 12.2 Hz); 6.75 (s, 1 H, H-2′); 6.77 (d, 1 H, H-a, *J* = 12.3 Hz,); 6.81 (d, 1 H, H-6 , *J* = 8.5 Hz); 6.84 (d, 1 H, H-5′, *J* = 8.6 Hz); 7.20 (d, 2 H, H-3, H-5, *J* = 5.4 Hz); 8.45 (d, 2 H, H-2, H-6, *J* = 5.5 Hz).

(*Z***-1)**·NH_4ClO_4: ^{1}H NMR (300.16 MHz, CD_3CN): δ = 3.56 (m, 8 H, 4 OCH_2); 3.59 (m, 4 H, 2 OCH_2); 3.77 and 3.88 (2 m, 4 H, 2 OCH_2); 4.16 (m, 4 H, 2 Ar$O\underline{CH_2}$); 6.95 (d, 1 H, H-5′, *J* = 8.5 Hz); 7.04 (d, 1 H, H-b, *J* = 16.5 Hz); 7.15 (d, 1 H, H-6′, *J* = 8.6 Hz); 7.21 (s, 1 H, H-2′); 7.39 (d, 1 H, H-a, *J* = 16.5 Hz); 7.47 (d, 2 H, H-3, H-5, *J* = 4.9 Hz); 8.46 (broad s, 2 H, H-2, H-6).

(*Z*-**1**)·**A5**: ^{1}H NMR (300.16 MHz, CD_3CN): δ = 1.26 (m, 2 H, CH_2 of **A5**); 1.46 (m, 4 H, 2CH_2 of **A5**); 2.19 (tr, 2 H, CH_2COOH of **A5**, *J* = 7.3 Hz); 2.80 (tr, 2 H, $CH_2NH_3^+$ of **A5**, *J* = 6.7 Hz); 3.65 (m, 4 H, 2 OCH_2); 3.67 (m, 4 H, 2 OCH_2); 3.68 (m, 4 H, 2 OCH_2); 3.74 and 3.85 (2 m, 4 H, 2 OCH_2); 3.92 and 4.20 (both m, 4 H, 2 Ar$O\underline{CH_2}$); 6.57 (d, 1 H, H-b, *J* = 11.6 Hz); 6.79 (d, 1 H, H-a, *J* = 12.2 Hz,); 6.82 (s, 1 H, H-2′); 6.88 (d, 1 H, H-6′, *J* = 8.5 Hz); 6.92 (d, 1 H, H-5′, *J* = 8.5 Hz); 7.20 (d, 2 H, H-3, H-5, *J* = 4.9 Hz); 8.46 (broad s, 2 H, H-2, H-6).

(*Z*-**1**)·**A10**: ^{1}H NMR (300.16 MHz, CD_3CN): δ = 1.26 (m, 8 H, 4CH_2 of **A10**); 1.42 (m, 4 H, 2CH_2 of **A10**); 1.55 (m, 4 H, 2CH_2 of **A10**); 2.23 (m, 2 H, $\underline{CH_2}COOH$ of **A10**); 2.80 (broad s, 2 H, $CH_2NH_3^+$ from **A10**); 3.66 (m, 4 H, 2 OCH_2); 3.68 (m, 4 H, 2 OCH_2); 3.69 (m, 4 H, 2 OCH_2); 3.76 and 3.86 (both m, 4 H, 2 OCH_2); 3.93 and 4.20 (both m, 4 H, 2 Ar$O\underline{CH_2}$); 6.57 (d, 1 H, H-b, *J* = 12.2 Hz); 6.80 (d, 1 H, H-a, *J* = 12.2 Hz,); 6.84 (s, 1 H, H-2′); 6.89 (d, 1 H, H-6′, *J* = 8.5 Hz); 6.93 (d, 1 H, H-5′, *J* = 8.5 Hz); 7.22 (broad s, 2 H, H-3, H-5); 8.46 (broad s, 2H, H-2, H-6).

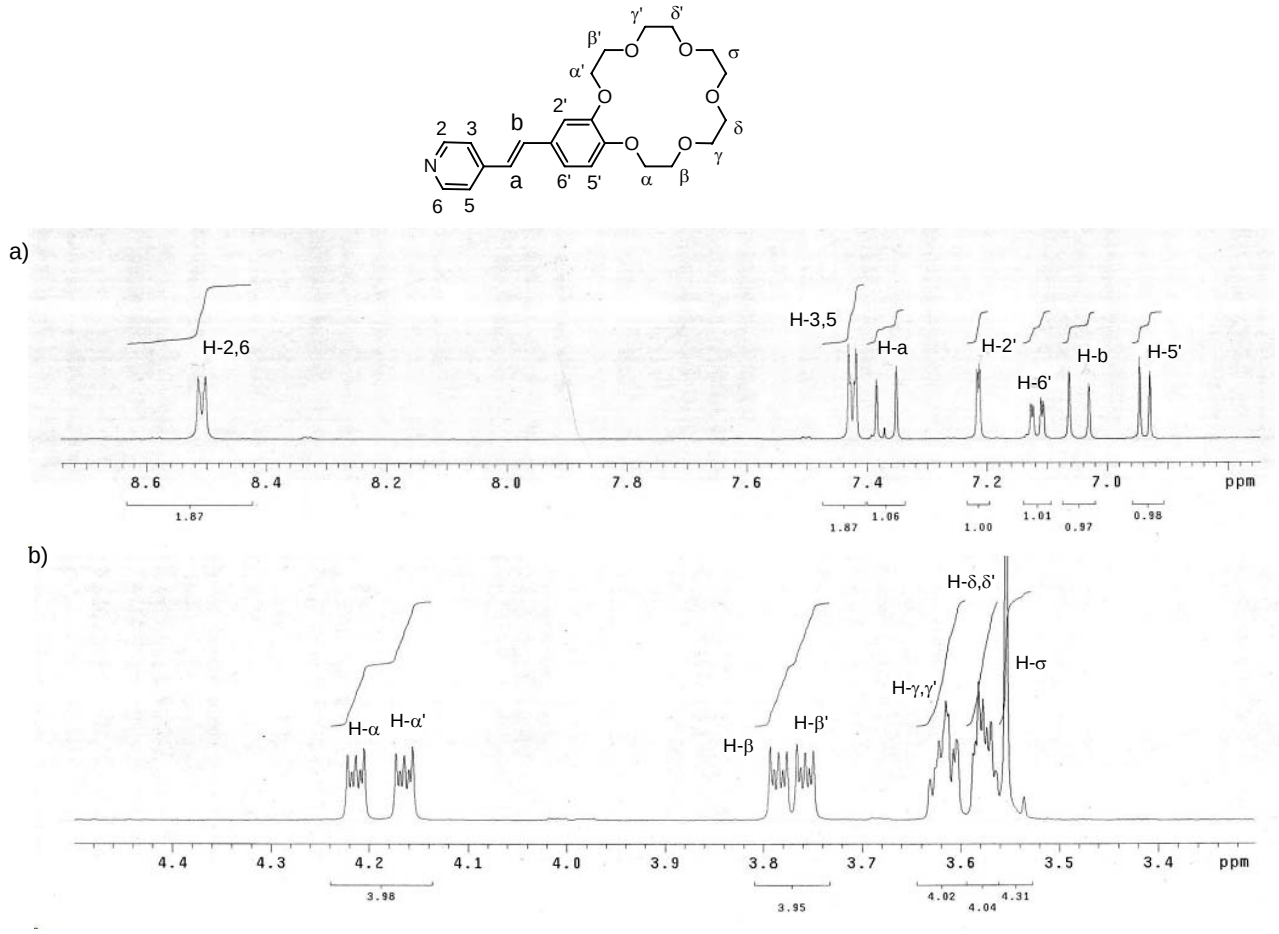

Fig. S7. ^{1}H NMR spectrum of *E*-**1** in CD_3CN at 295 K.

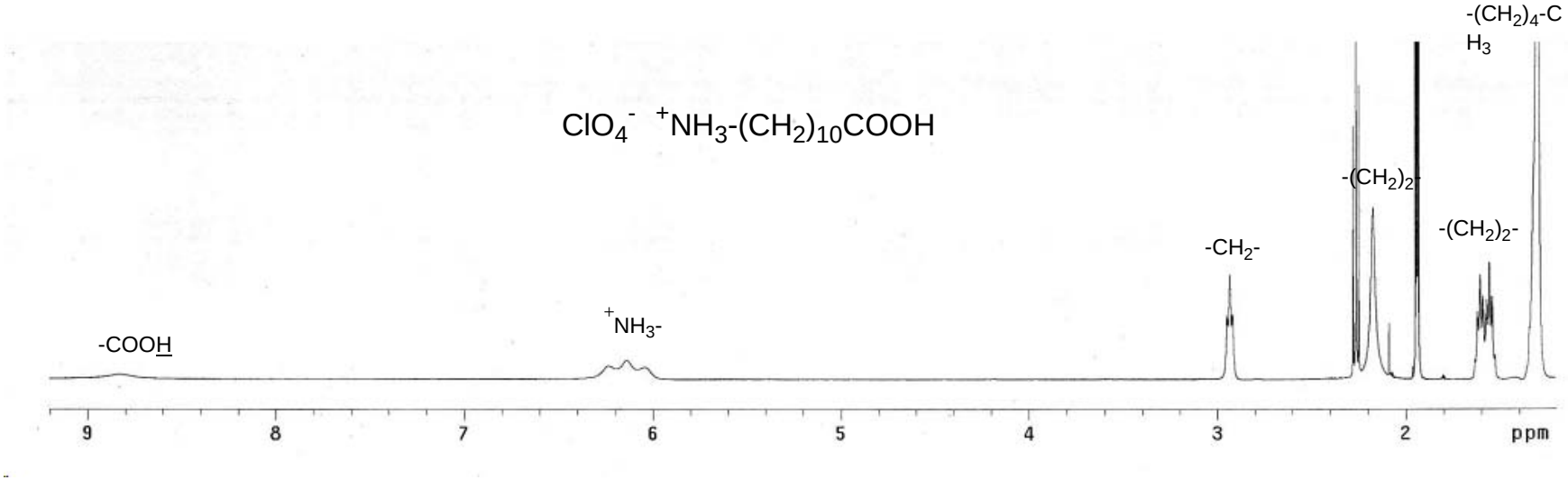

Fig. S8. ^{1}H NMR spectrum of **A10** in CD_3CN at 295 K.

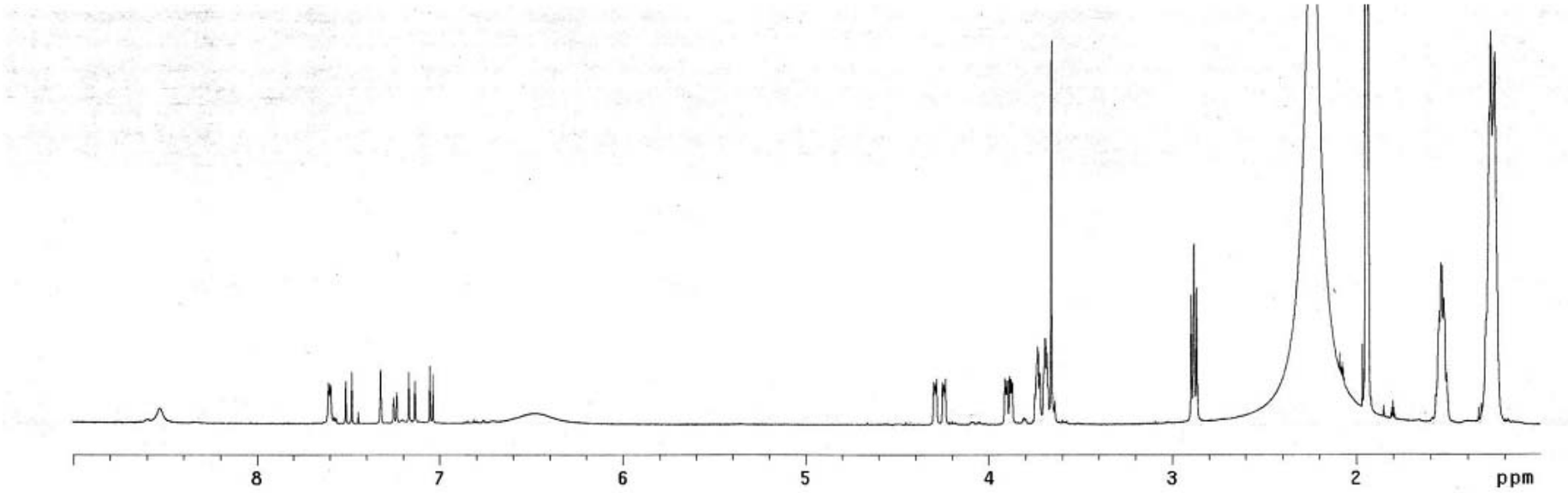

Fig. S9. ^{1}H NMR spectrum of complex *E*-**1**·**A10** in CD_3CN at 295 K.

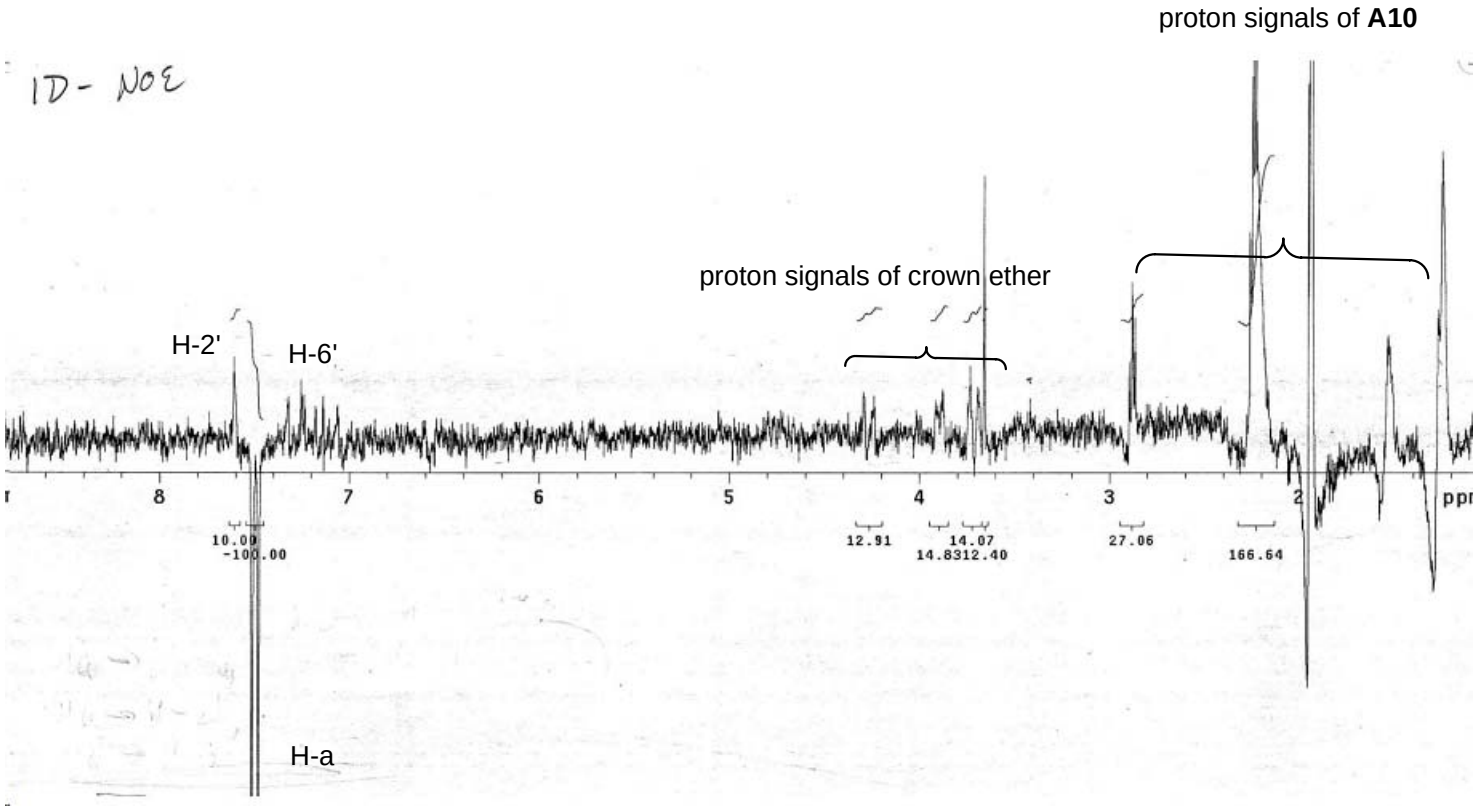

Fig. S10. ^{1}H NMR spectrum (1D-NOE) of complex *E*-**1**·**A10** in CD_3CN at 295 K. Excitation of H-a gives enhanced absorption at H-2', H-6' and at the crown ether protons of *E*-**1** and more pronounced enhanced absorption at the methylene protons of **A10**.

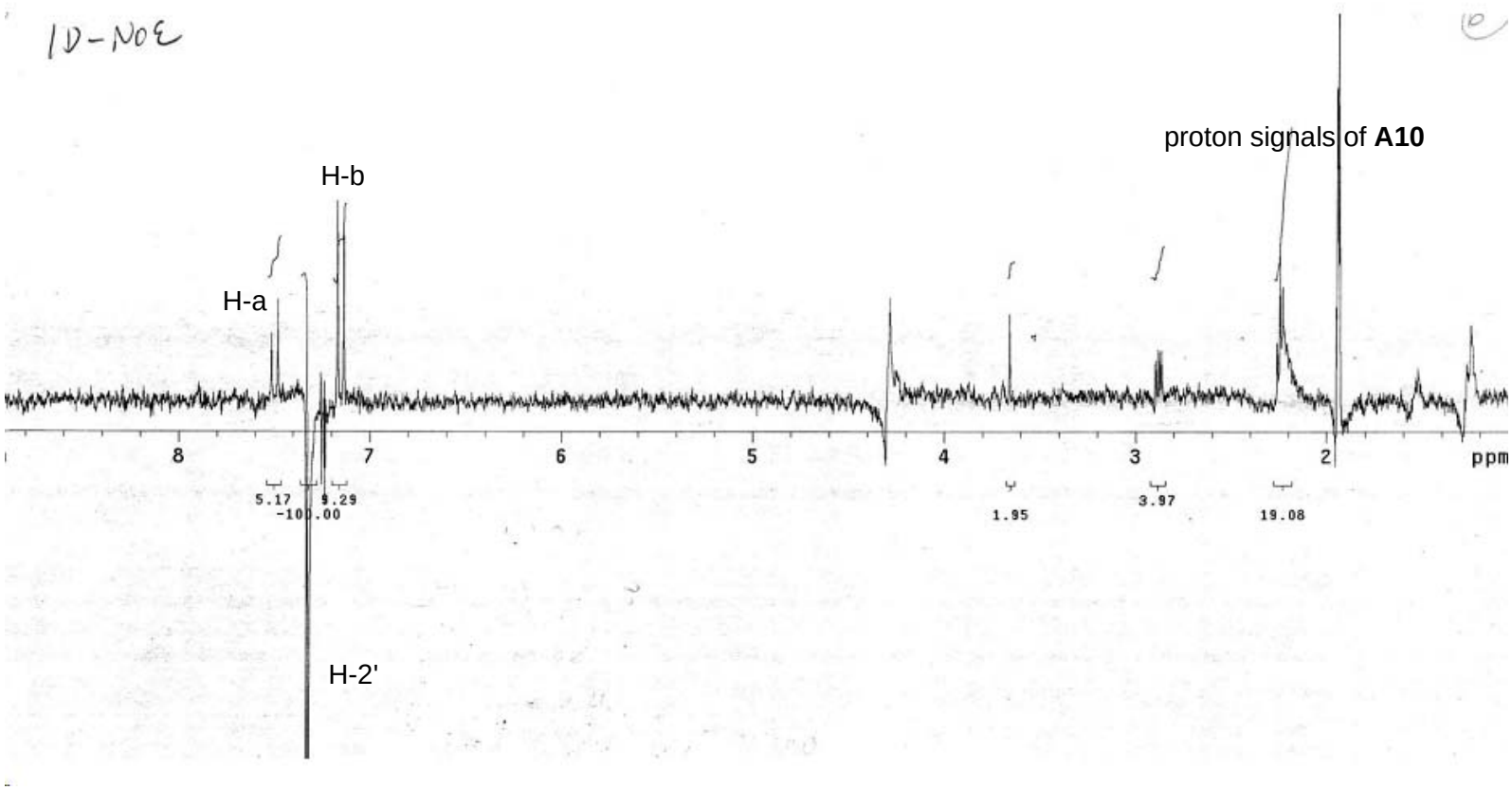

Fig. S11. ^{1}H NMR spectrum (1D-NOE) of complex *E*-**1**·**A10** in CD_3CN at 295 K. Excitation of H-2' gives enhanced absorption for the H-a and H-b protons of *E*-**1**, and for the methylene protons of **A10**.

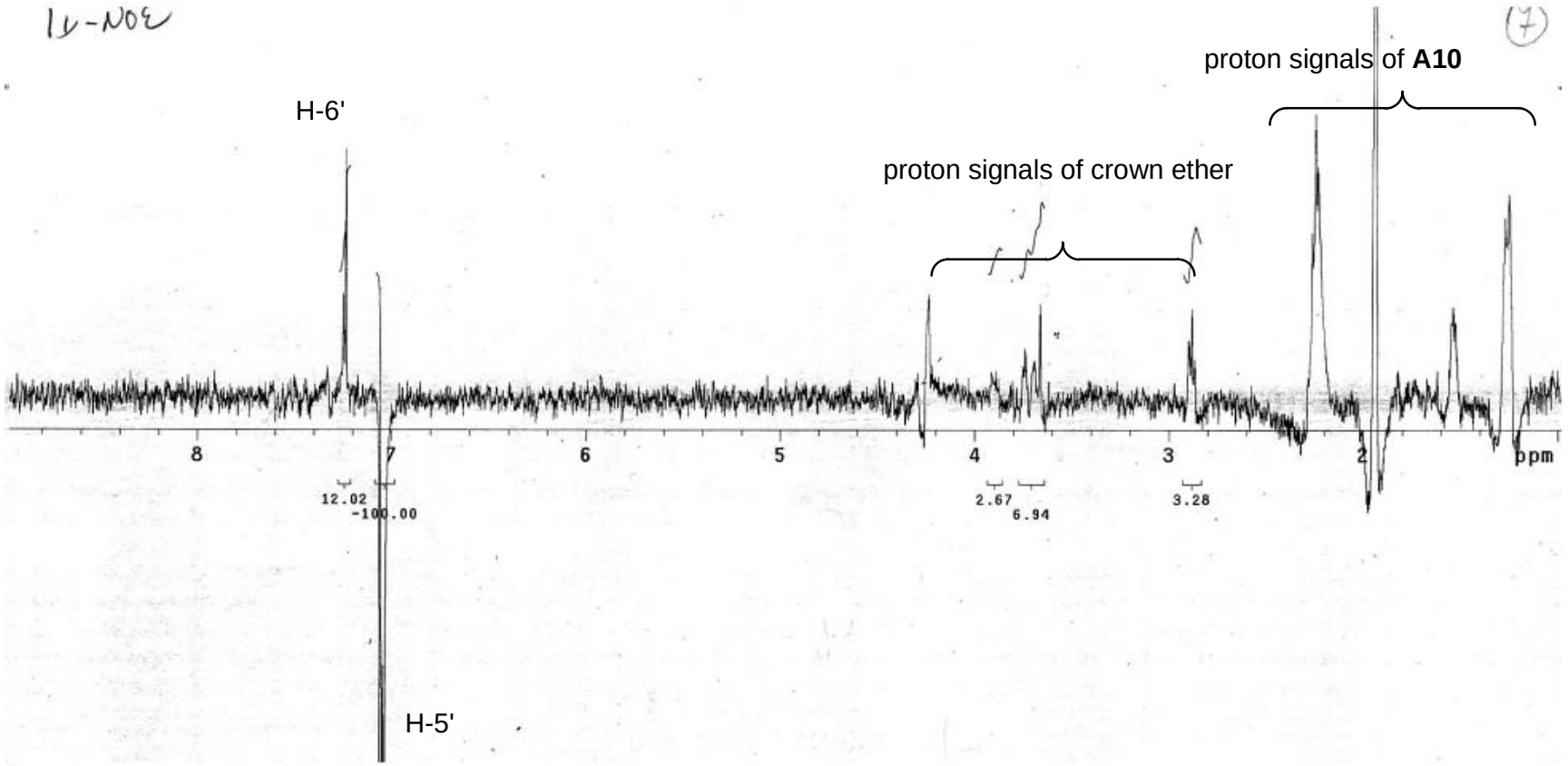

Fig. S12. ^{1}H NMR spectrum (1D-NOE) of complex *E*-**1**·**A10** in CD_3CN at 295 K. Excitation of H-5' gives enhanccd absorption at H-6' and the crown ether protons of *E*-**1** and at the methylene protons of **A10**.

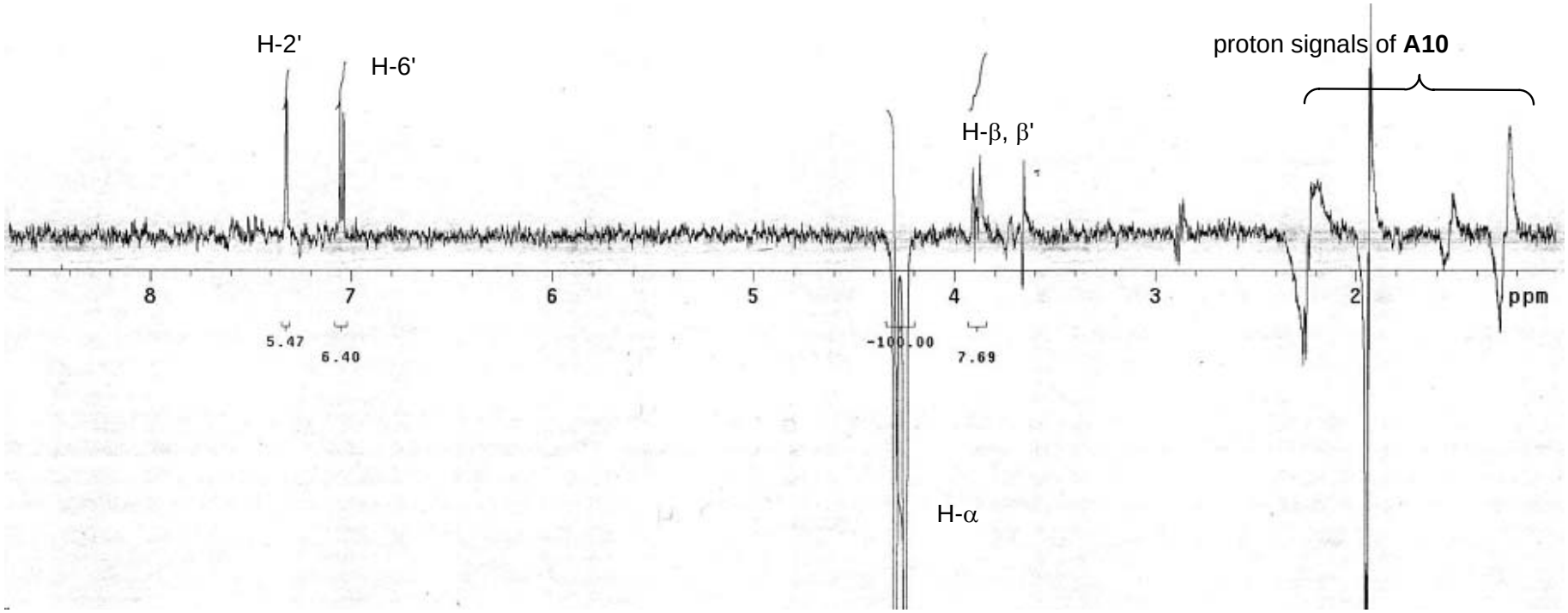

Fig. S13. ^{1}H NMR spectrum (1D-NOE) of complex *E*-**1**·**A10** in CD_3CN at 295 K. Excitation of the H-α and H-α' protons of *E*-**1** gives enhanced absorption at the H-2', H-6', H-β and H-β' protons of *E*-**1** and little, if any, response at the methylene protons of **A10** (derivative type signals in that region are due to a small shift between spectra with and without excitation at H-α and H-α').

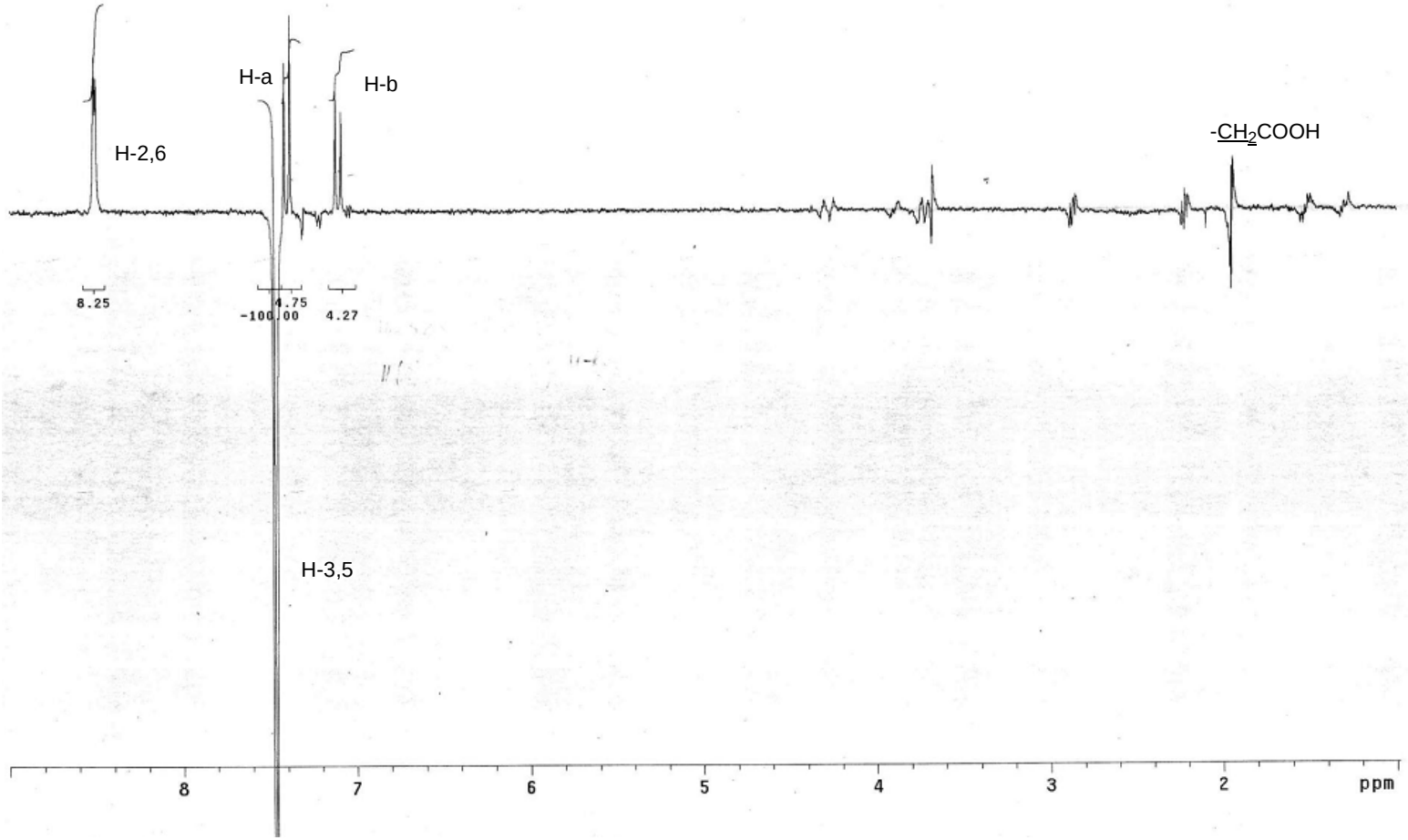

Fig. S14. ^{1}H NMR spectrum (1D-NOE) of complex *E*-**1**·**A10** in CD_3CN at 295 K. Excitation at H-3,5, the meta pyridyl proton of *E*-**1** gives no enhanced absorption in the region of **A10** methylene proton signals.

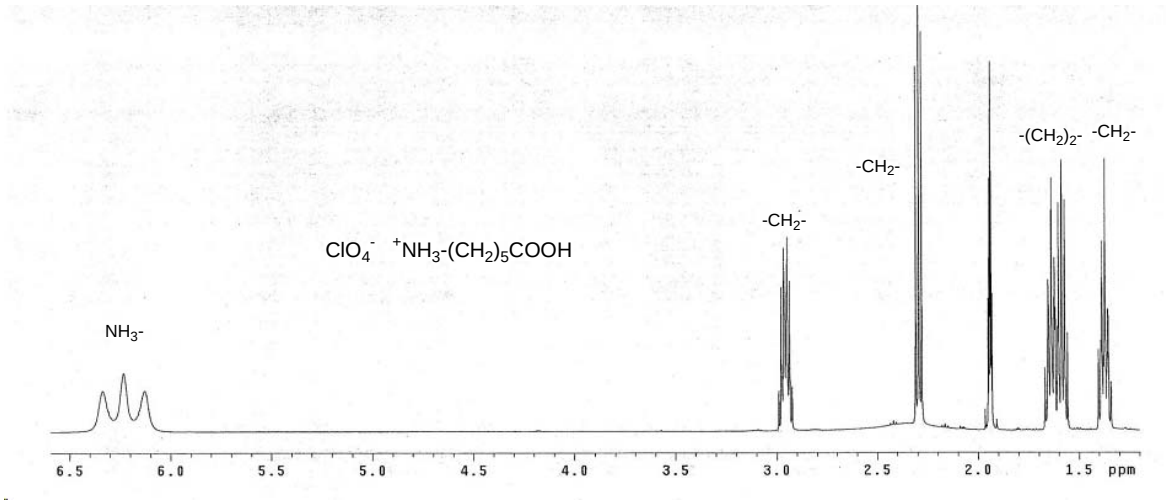

Fig. S15. ^{1}H NMR spectrum of **A5** in CD_3CN at 295 K.

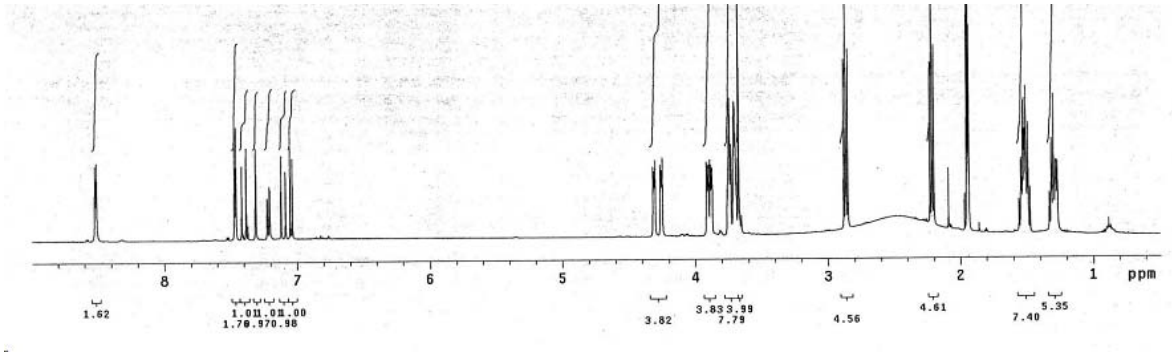

Fig. S16. ^{1}H NMR spectrum of complex *E*-**1**·**A5** in CD_3CN at 295 K.

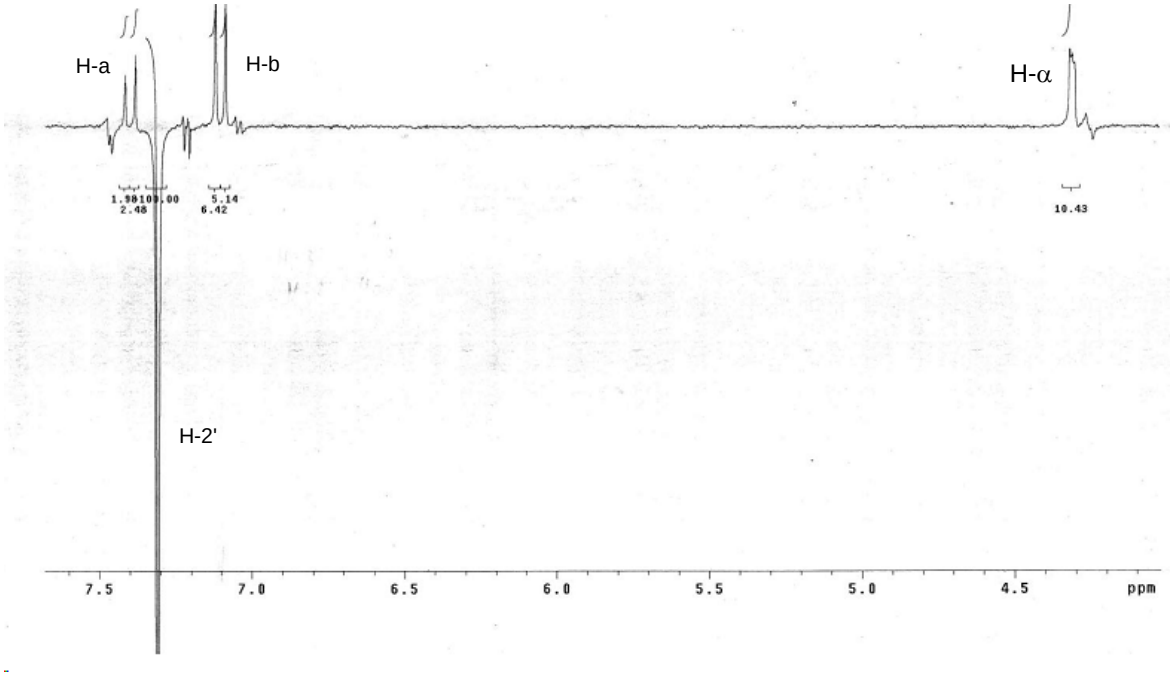

Fig. S17. ^{1}H NMR spectrum (1D-NOE) of complex *E*-**1**·**A5** in CD_3CN at 295 K. Excitation of H-2' gives enhanced absorption at H-a , H-b and tH-α protons of *E*-**1**.

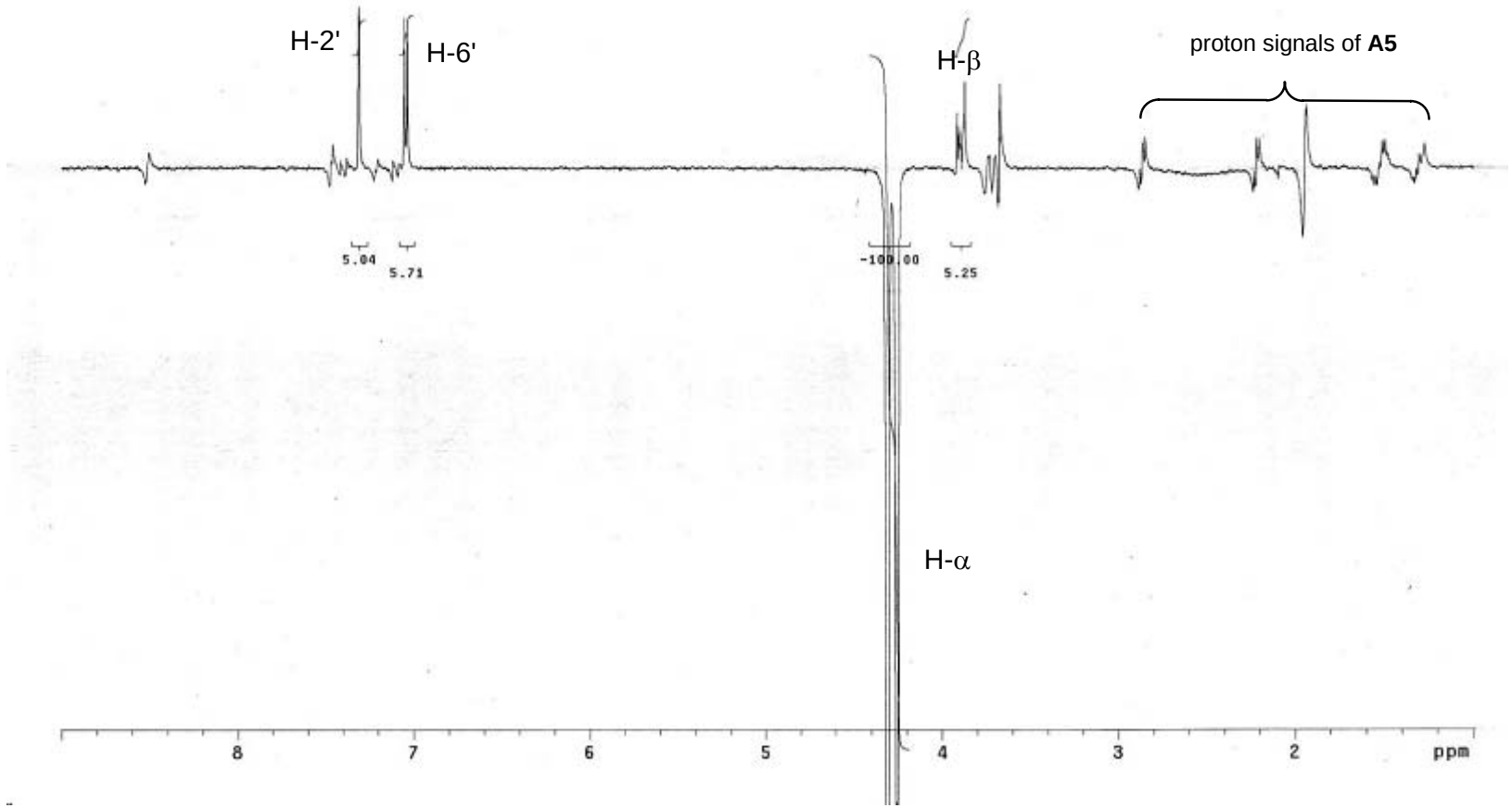

Fig. S18. ^{1}H NMR spectrum (1D-NOE) of complex *E*-**1**·**A5** in CD_3CN at 295 K. Excitation of the H-α and H-α' protons of *E*-**1** gives enhanced absorption for the H-2', H-6' and H-β protons of *E*-**1** and a smaller response at the methylene protons of **A5** (derivative type signals in that region are due to a small shift between spectra with and without excitation at H-α and H-α').

The following figures concern the interaction of 4-methylpyridine (MePy) with acetic acid in CD_3CN at 295 K. Note the disappearance of the carboxylic proton at ~9 d in the ^1H NMR spectrum of the 1:1 mixture.