Electronic Supplementary Information

Cyclen derivatives with two *trans*-methylnitrophenolic pendant arms: structural study of their copper(II) and zinc(II) complexes

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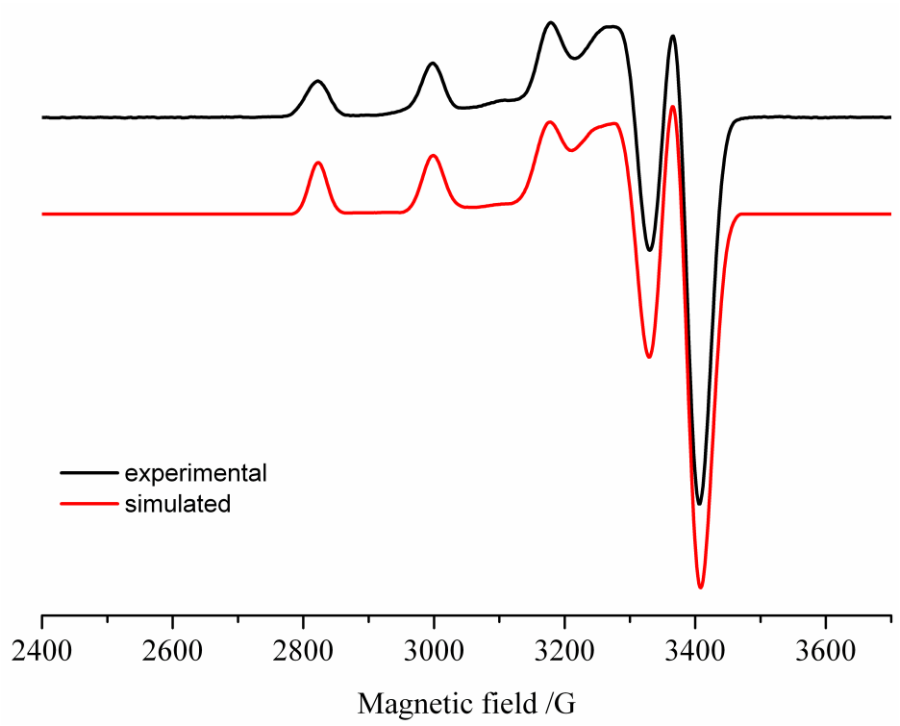

Fig. S1 Experimental and simulated X-band EPR spectrum of [Cu(do2nph)] complex. The spectrum was recorded in DMSO/H_2O (9:1) at a microwave power of 2.0 mW, frequency (ν) 9.51 GHz, and T = 90 K.

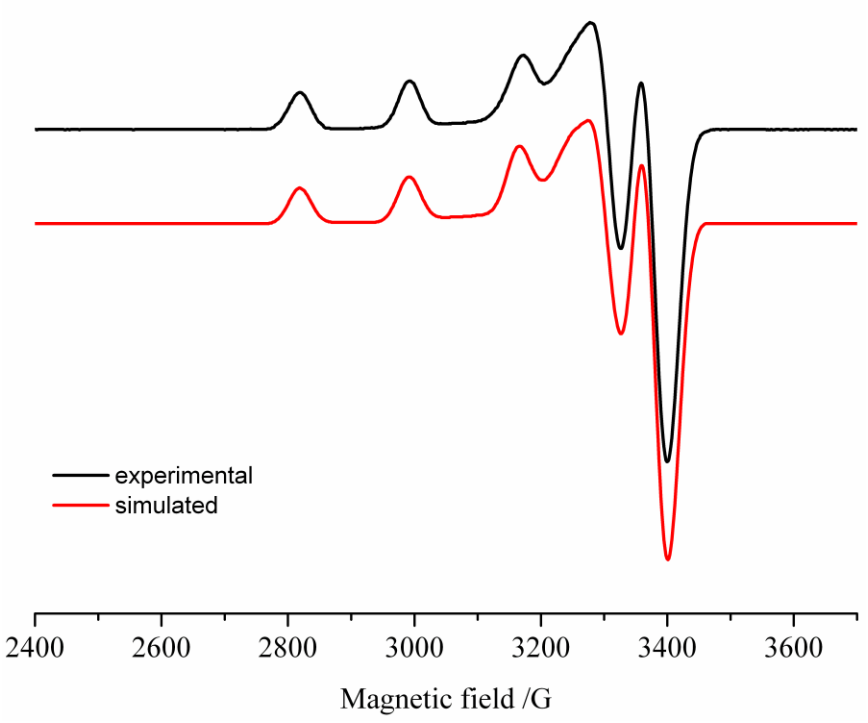

Fig. S2 Experimental and simulated X-band EPR spectrum of $[Cu(Hdo2nph)]^+$. The spectrum was recorded in DMSO/H_2O (9:1) at a microwave power of 2.0 mW, frequency (ν) 9.51 GHz, and T = 90 K.

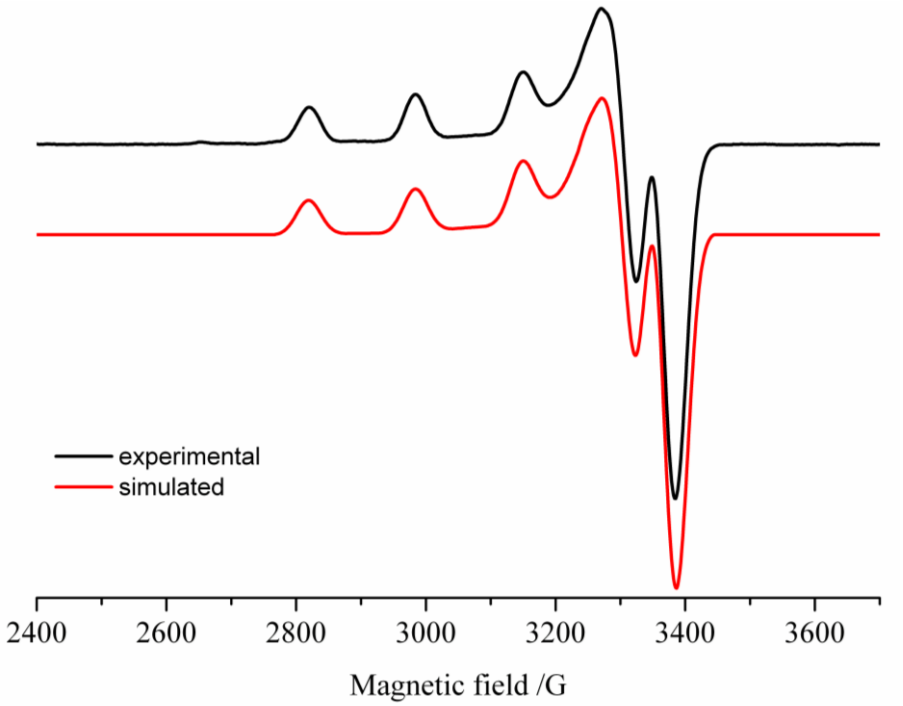

Fig. S3 Experimental and simulated X-band EPR spectrum of $[Cu(H_2do2nph)]^{2+}$. The spectrum was recorded in DMSO/H_2O (9:1) at a microwave power of 2.0 mW, frequency (ν) 9.51 GHz, and T = 90 K.

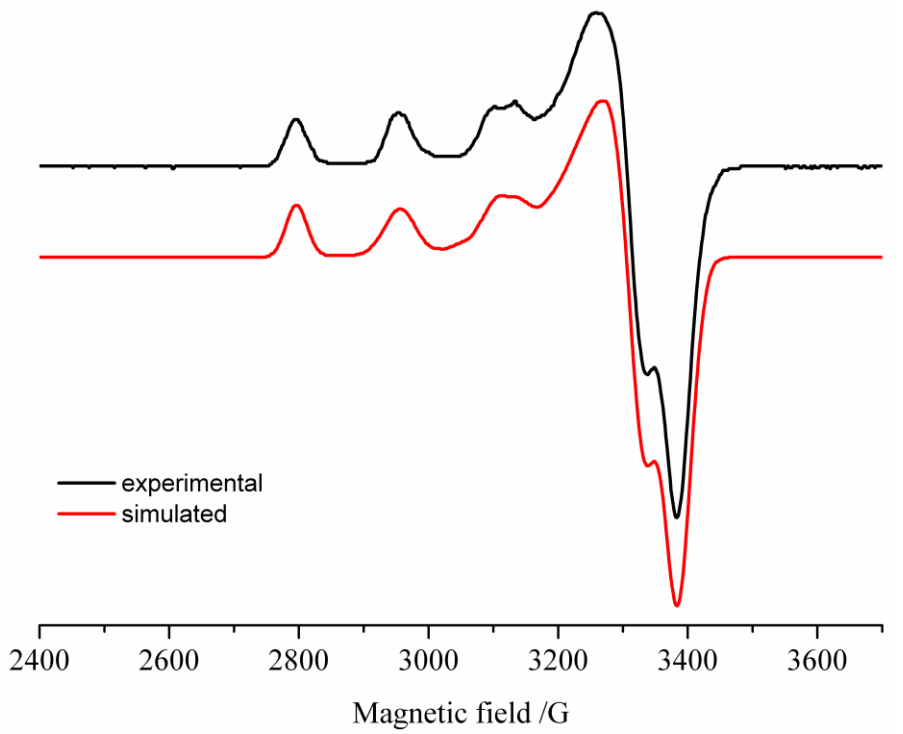

Fig. S4 Experimental and simulated X-band EPR spectrum of [Cu(cb-do2nph)]. The spectrum was recorded in DMSO/H_2O (9:1) at a microwave power of 2.0 mW, frequency (ν) 9.51 GHz, and T = 90 K.

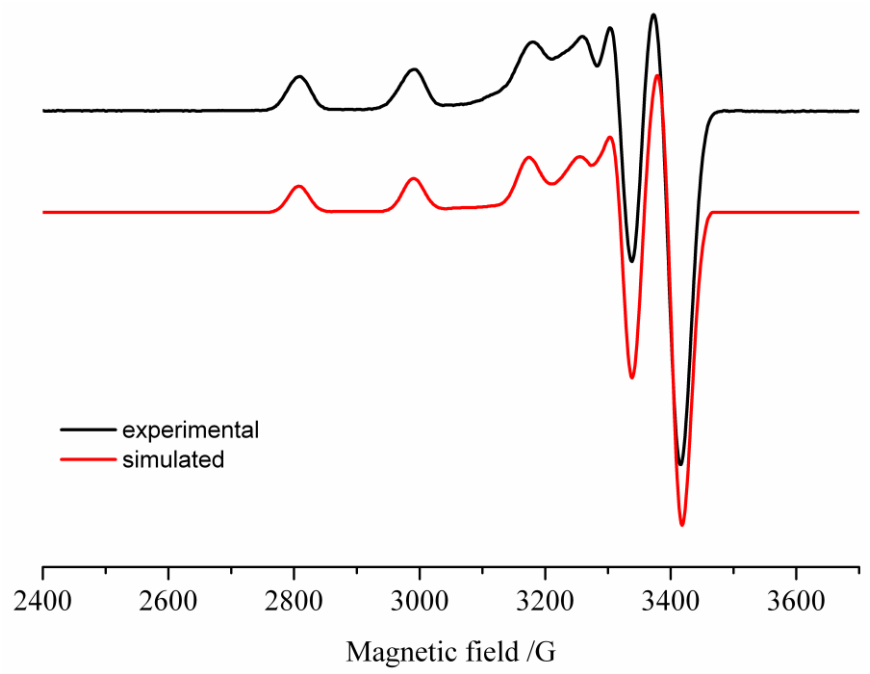

Fig. S5 Experimental and simulated X-band EPR spectrum of $[Cu(Hcb\text{-}do2nph)]^{+}$. The spectrum was recorded in DMSO/H_2O (9:1) at a microwave power of 2.0 mW, frequency (ν) 9.51 GHz, and T = 90 K.

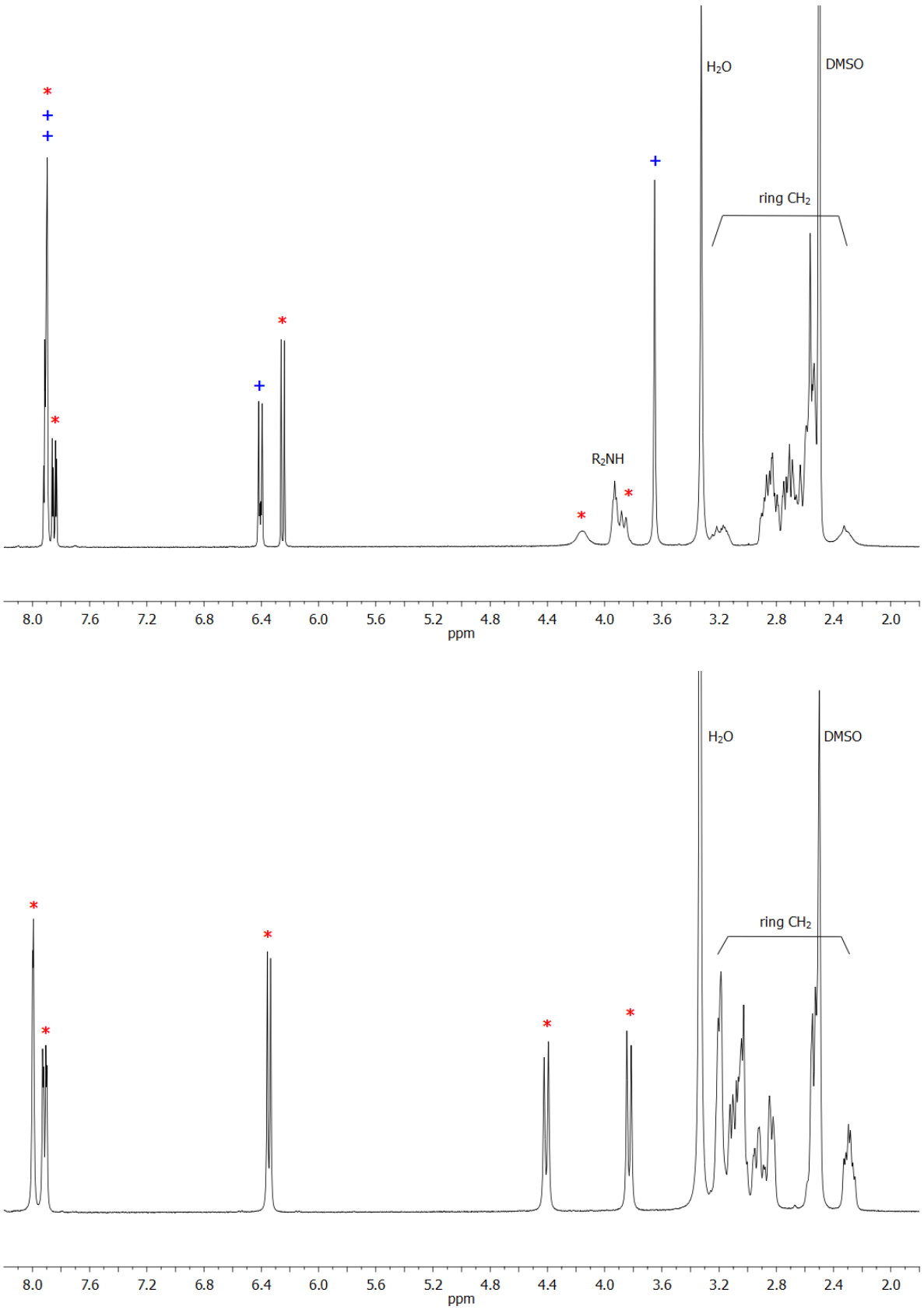

Fig. S6 ^{1}H NMR spectra of the zinc(II) complexes of do2nph (top) and cb-do2nph (bottom) in DMSO-*d*6, with labelling of the coordinated pendant arm resonances (*****) and uncoordinated ones (+).

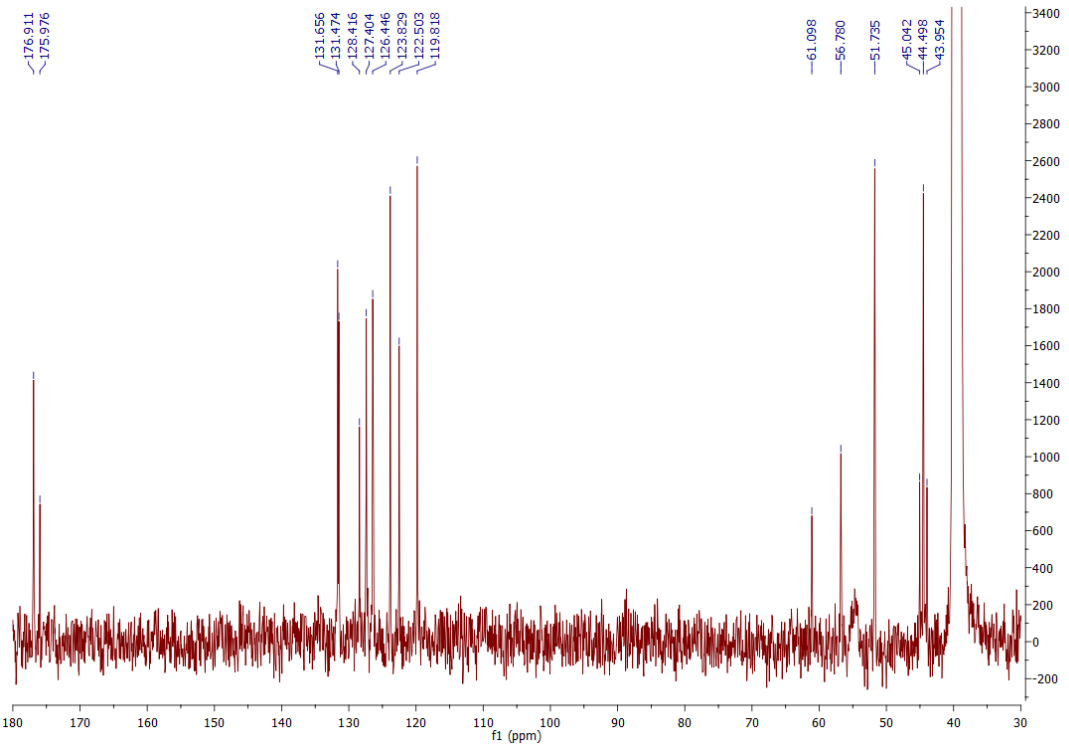

Fig. S7 ^{13}C NMR spectrum of the zinc(II) complex of H_2do2nph in DMSO-*d*6.

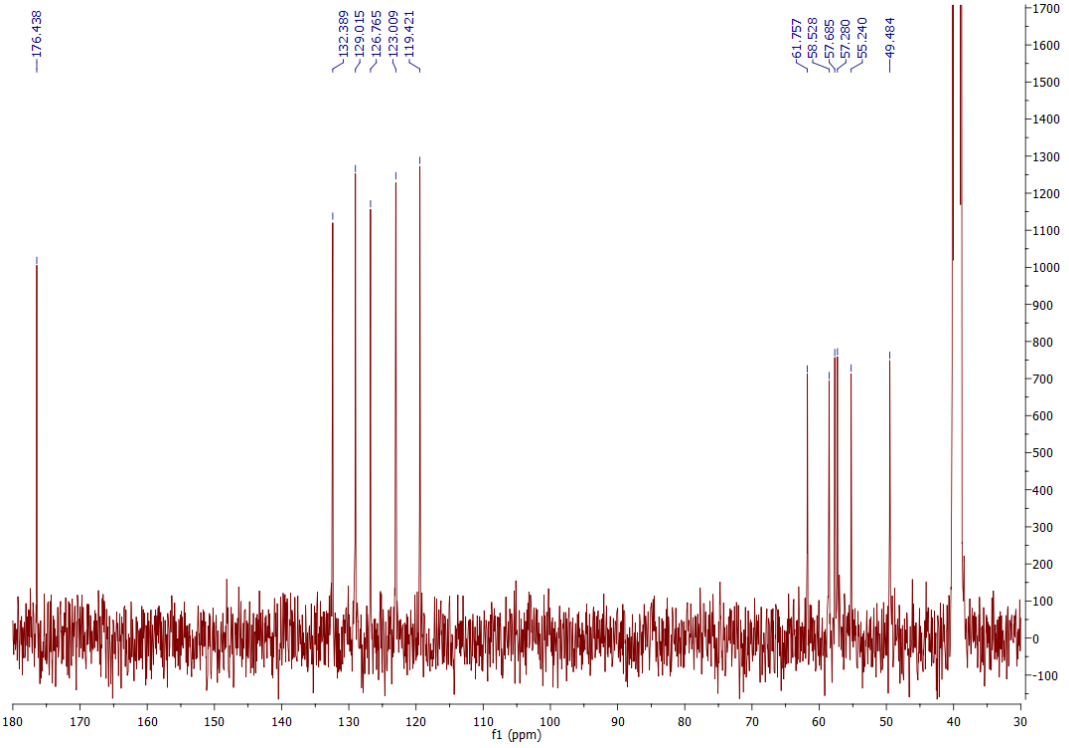

Fig. S8 ^{13}C NMR spectrum of the zinc(II) complex of H_2cb-do2nph in DMSO-*d*6.

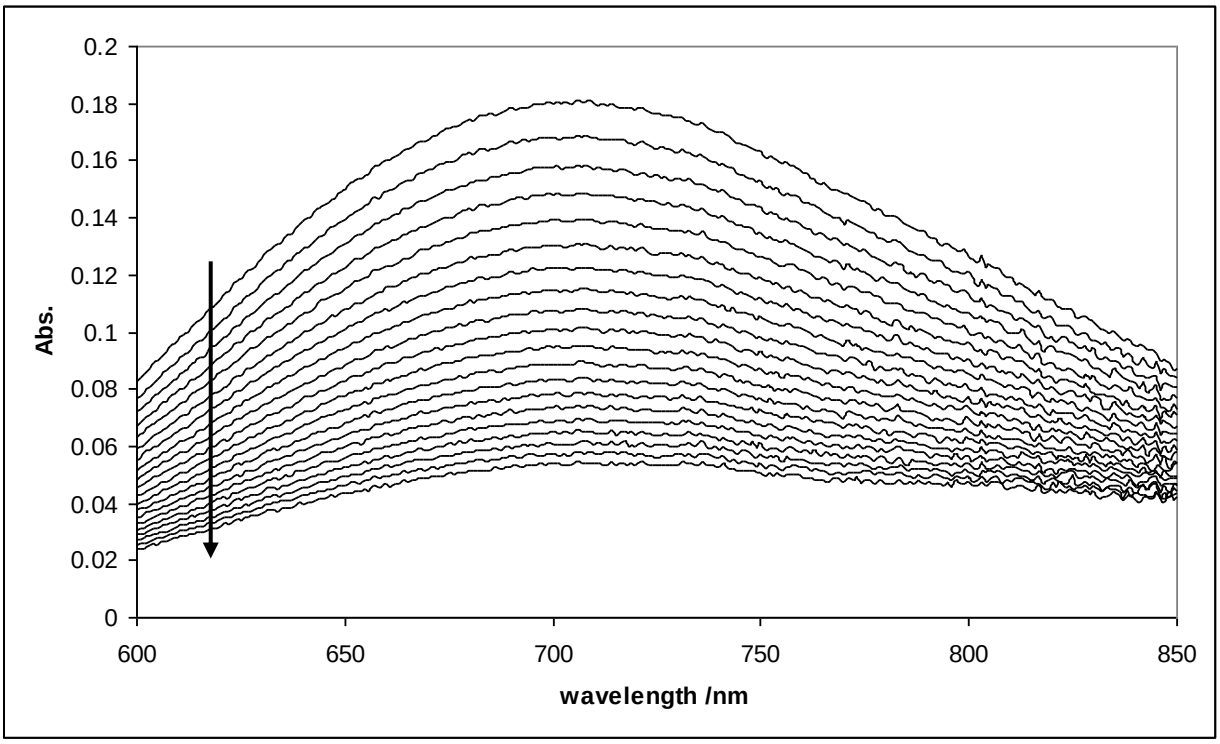

Fig. S9 Time course of the dissociation of the copper(II) complex of H_2-do2nph in 1 mol dm^{-3} HCl DMSO/H_2O 9:1 (v/v) solution at 298.2 K, followed at 1 min intervals.

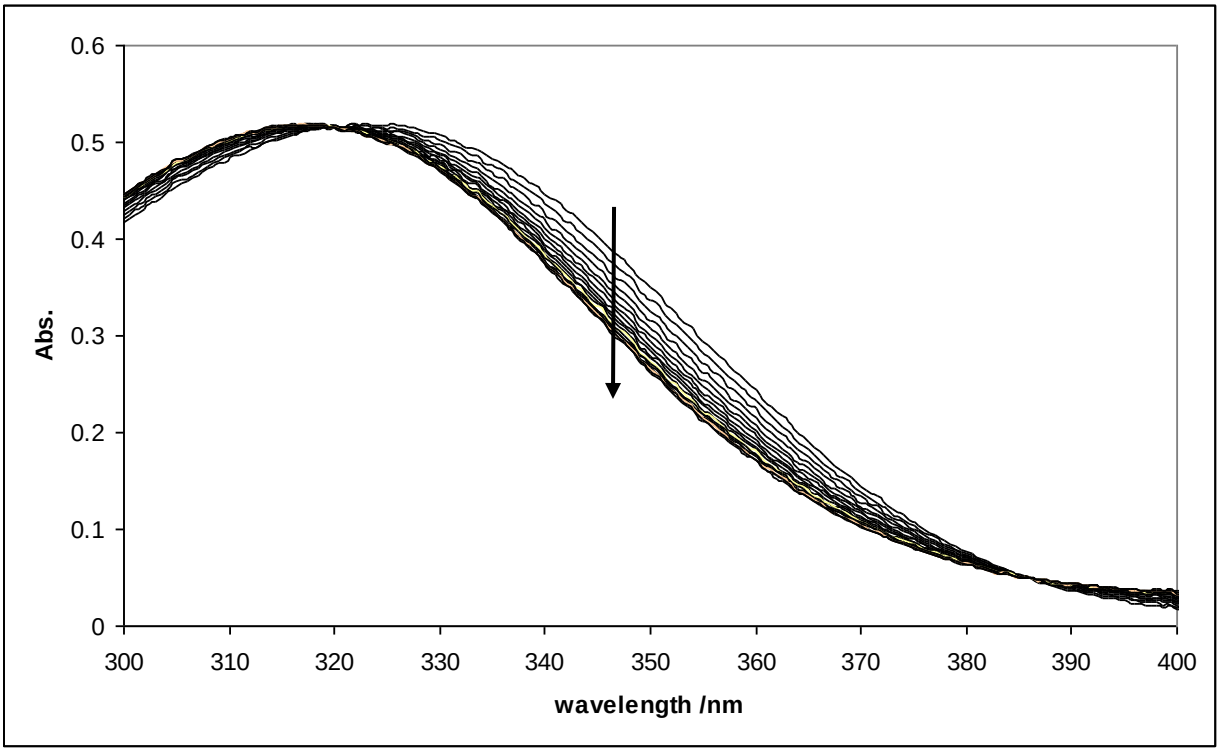

Fig. S10 Time course of the dissociation of the copper(II) complex of H_2cb-do2nph in 1 mol dm^{-3} HCl DMSO/H_2O 9:1 (v/v) solution at 298.2 K, followed at 10 min intervals.

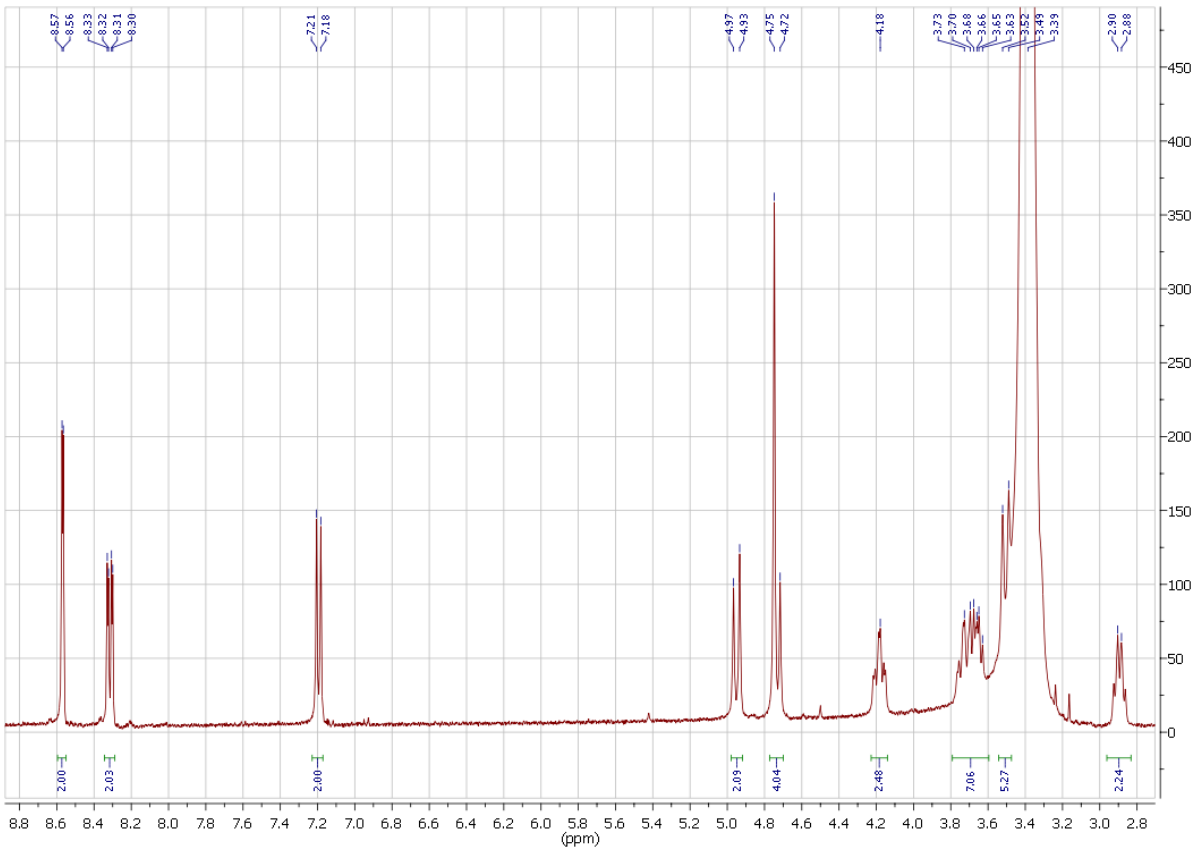

Fig. S11 ^{1}H NMR spectrum of diammonium salt (3) in DMSO-*d*6.

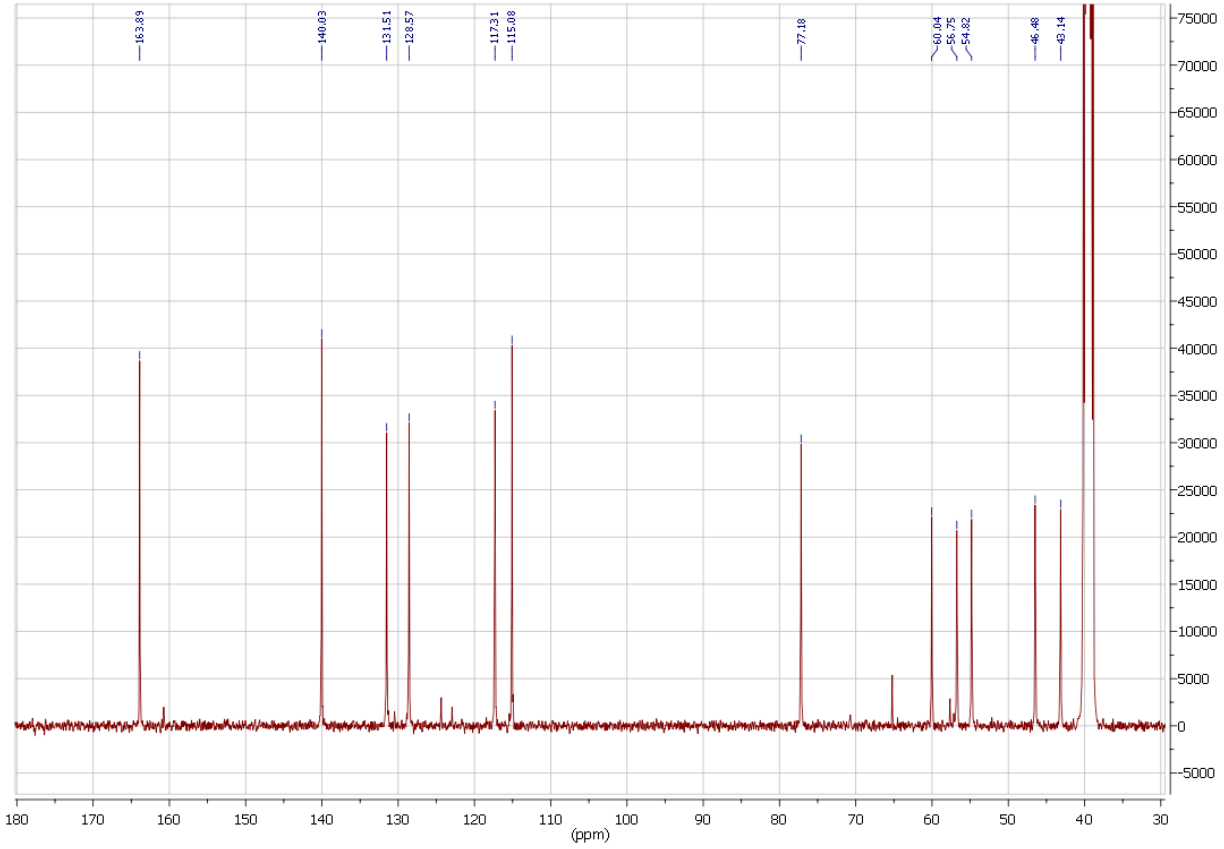

Fig. S12 ^{13}C NMR spectrum of diammonium salt (3) in DMSO-*d*6.

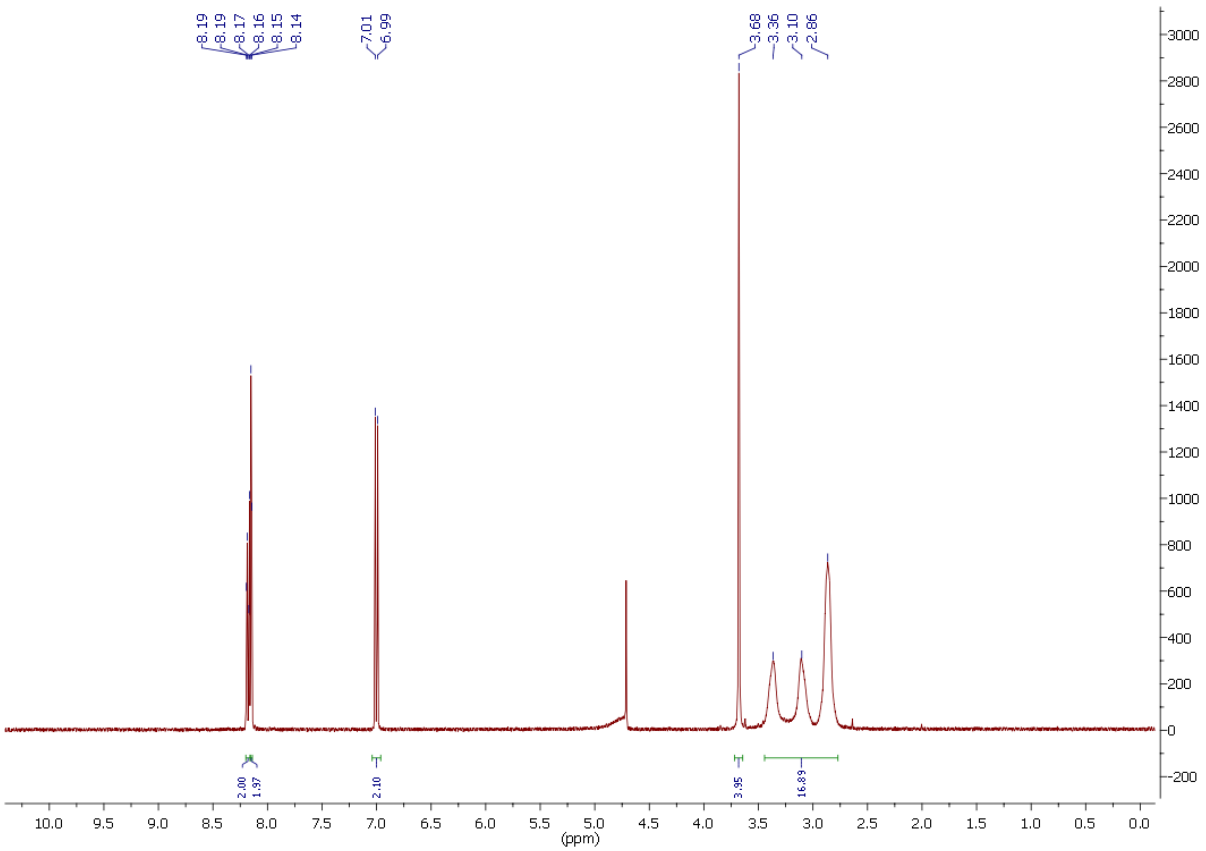

Fig. S13 ^{1}H NMR spectrum of do2nph in D_2O.

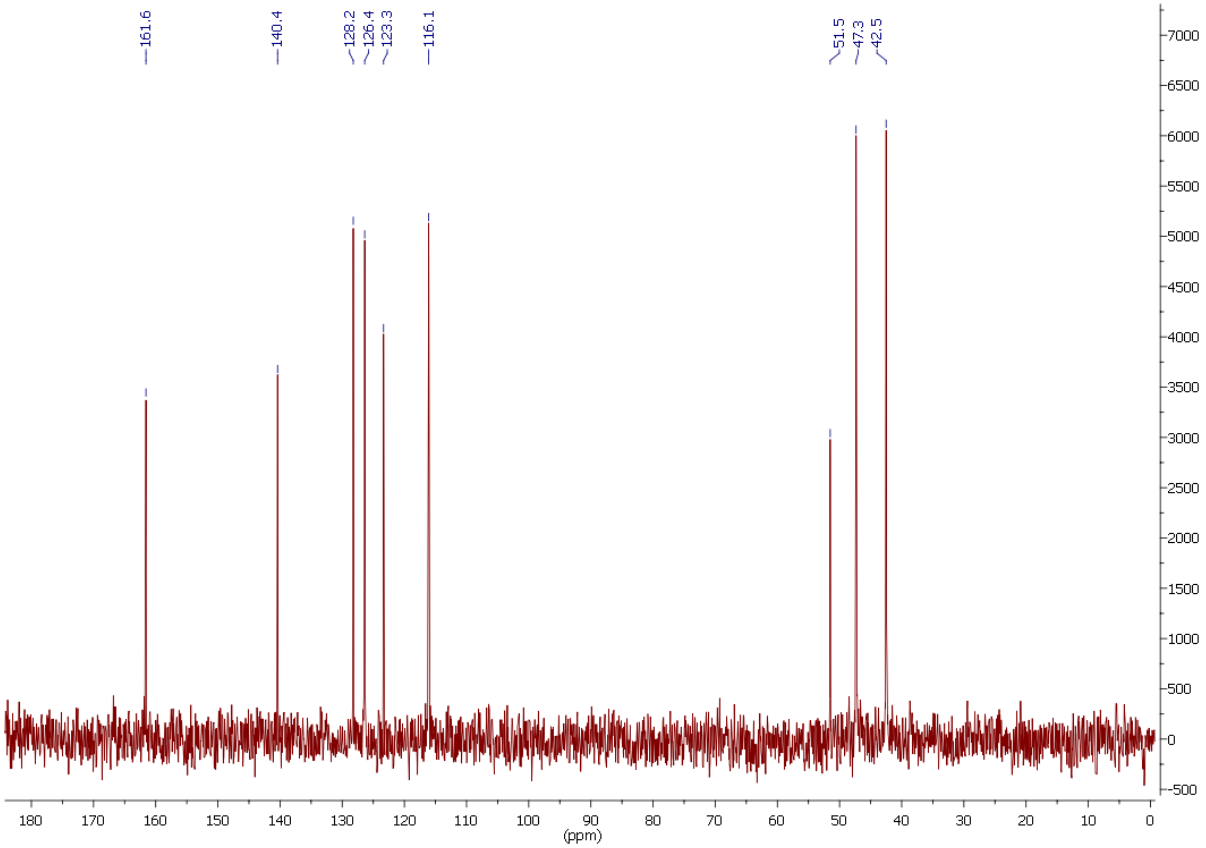

Fig. S14 ^{13}C NMR spectrum of do2nph in D_2O.

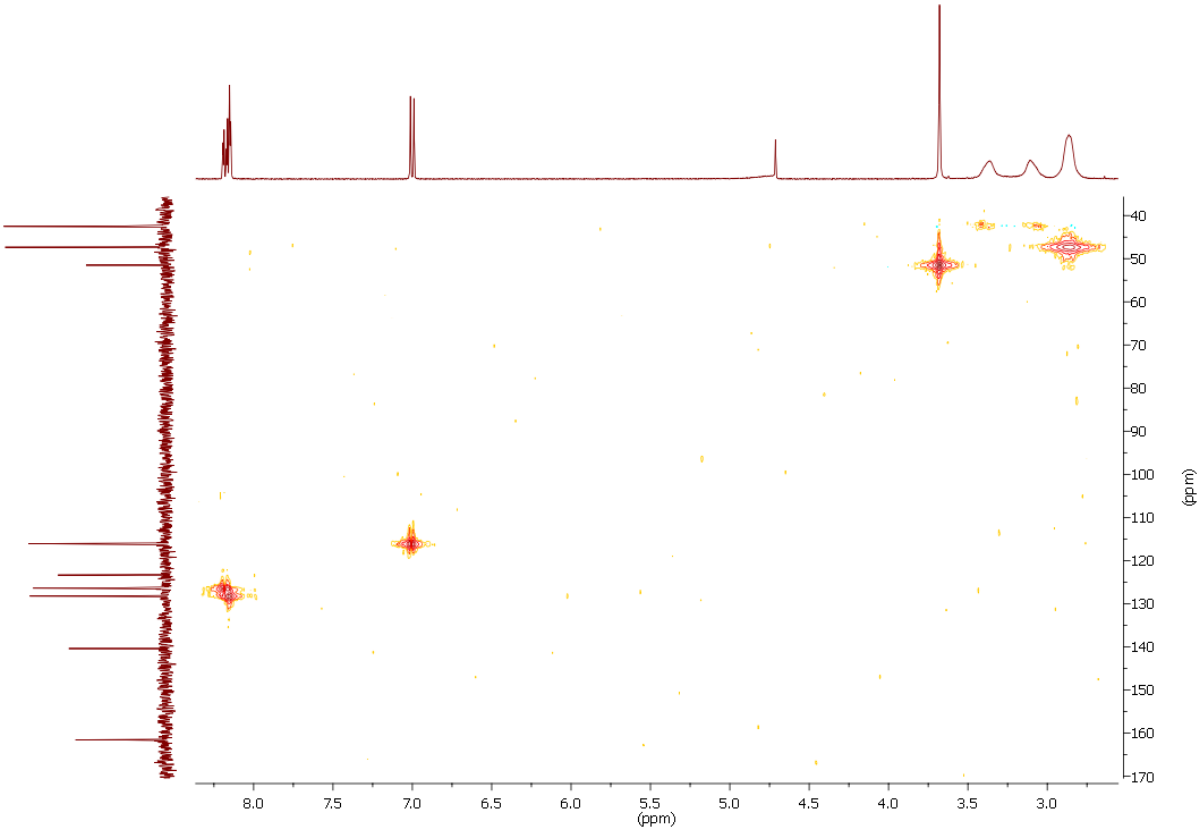

Fig. S15 HMQC spectrum of do2nph in D_2O.

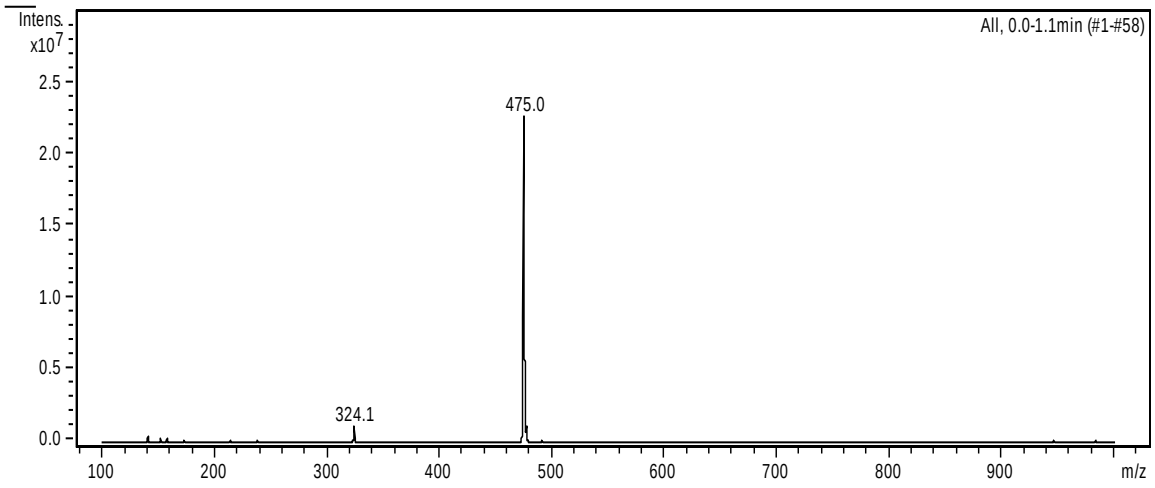

Fig. S16 ESI mass spectrum of do2nph in H_2O/MeOH (9:2).

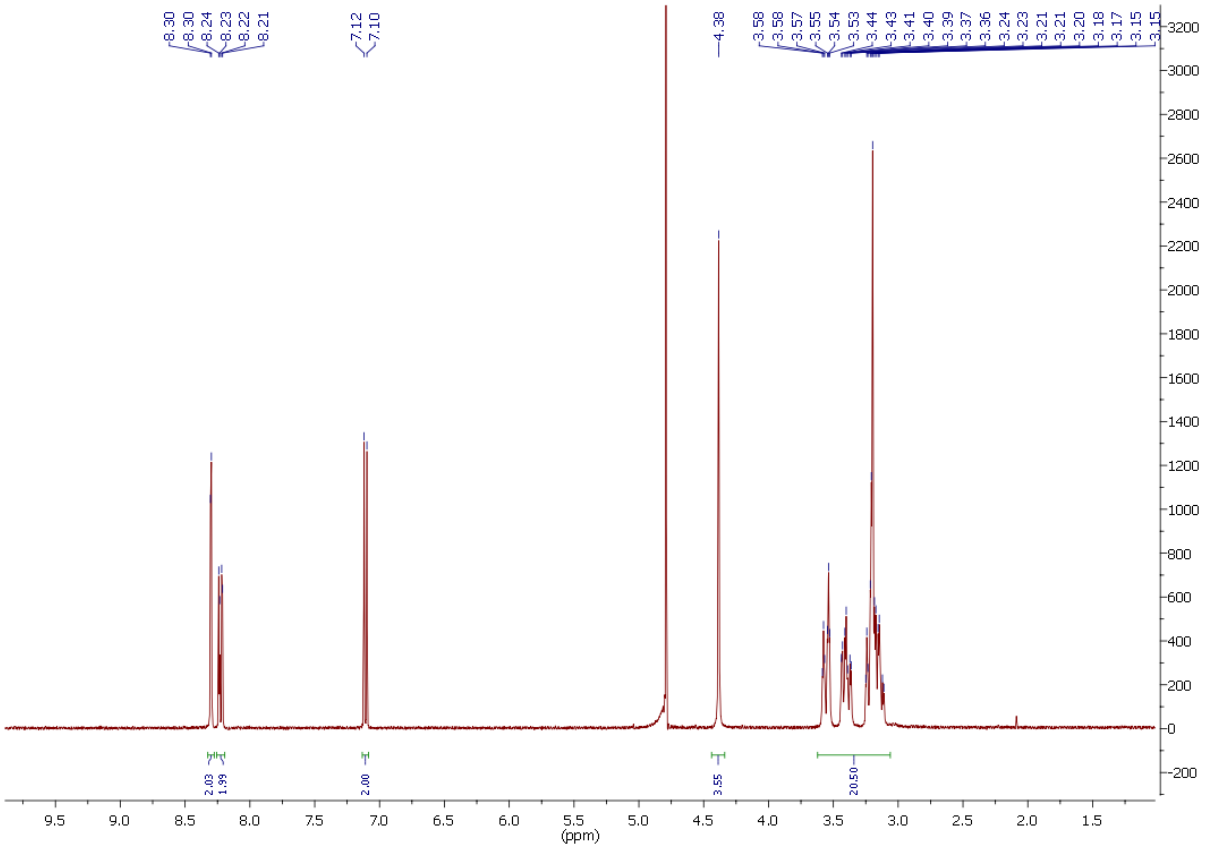

Fig. S17 ^{1}H NMR spectrum of cb-do2nph in D_2O.

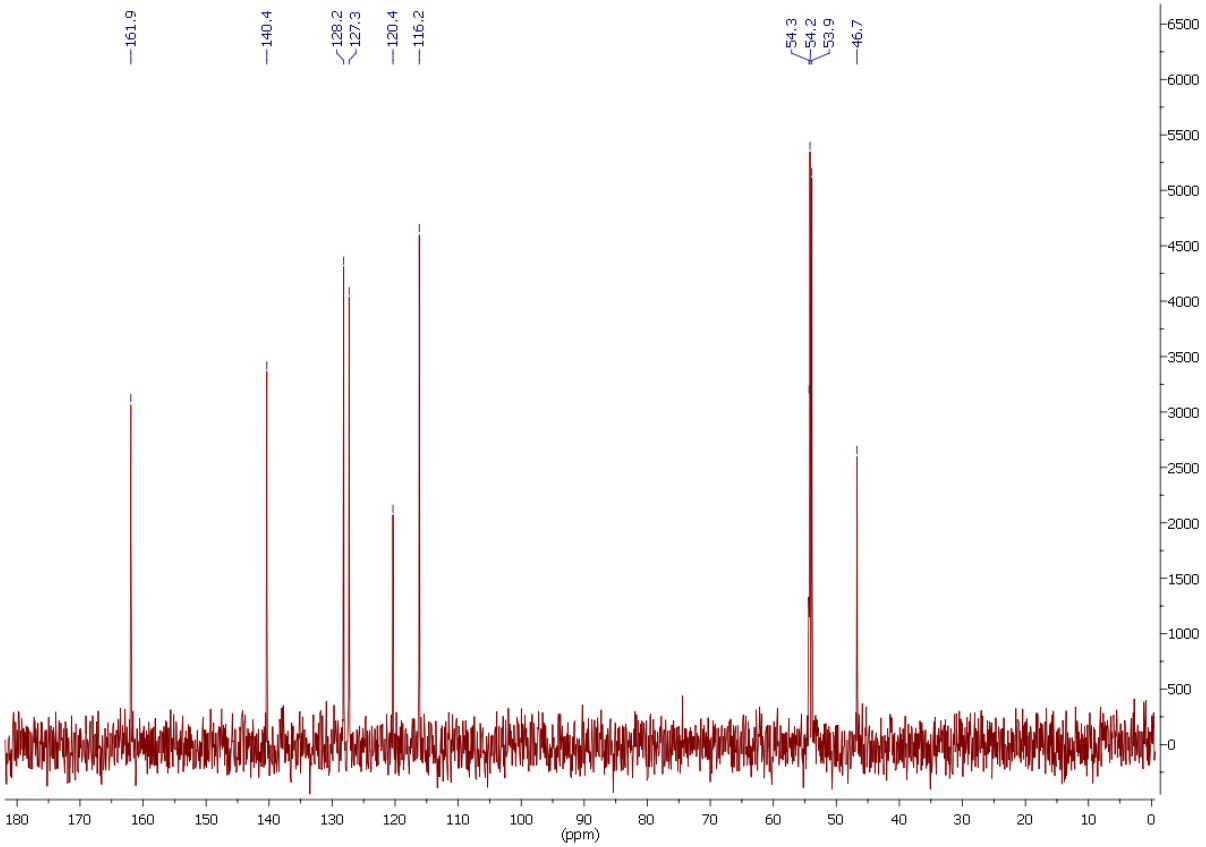

Fig. S18 ^{13}C NMR spectrum of cb-do2nph in D_2O.

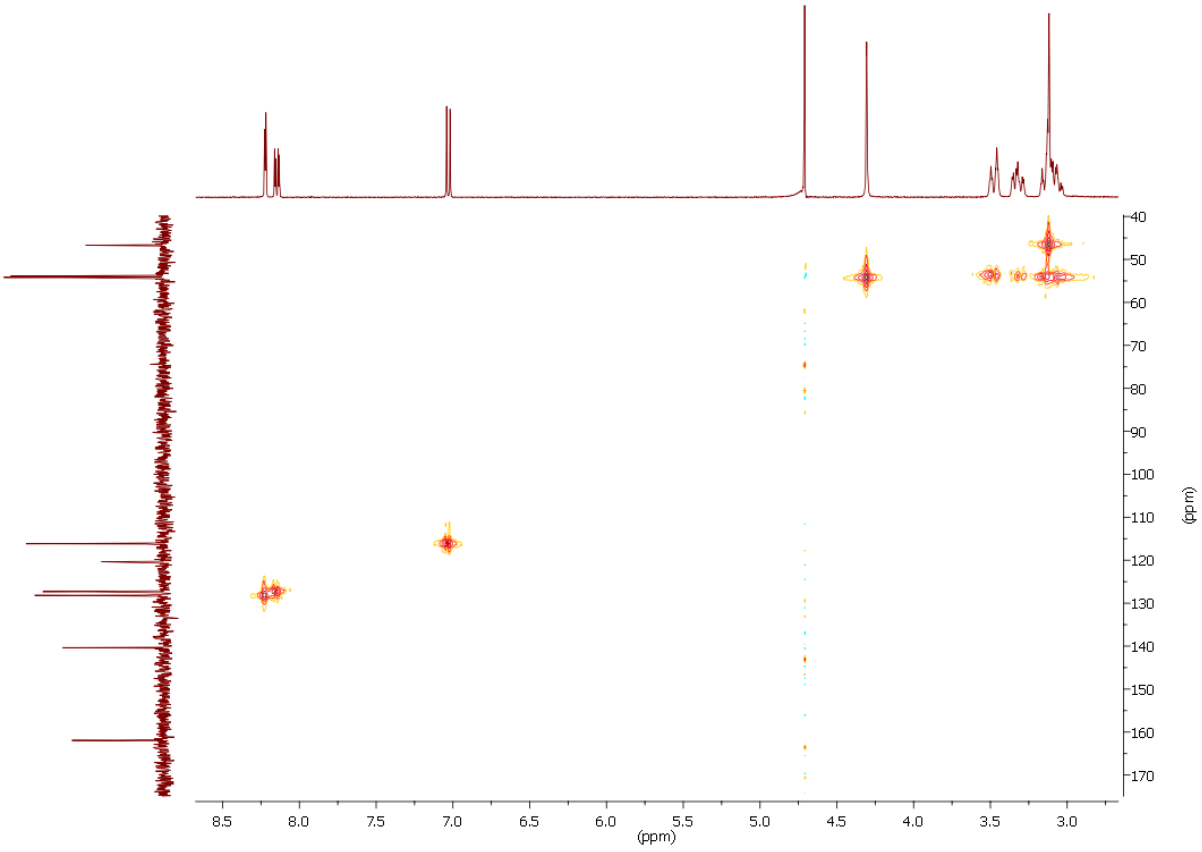

Fig. S19 HMQC spectrum of cb-do2nph in D_2O.

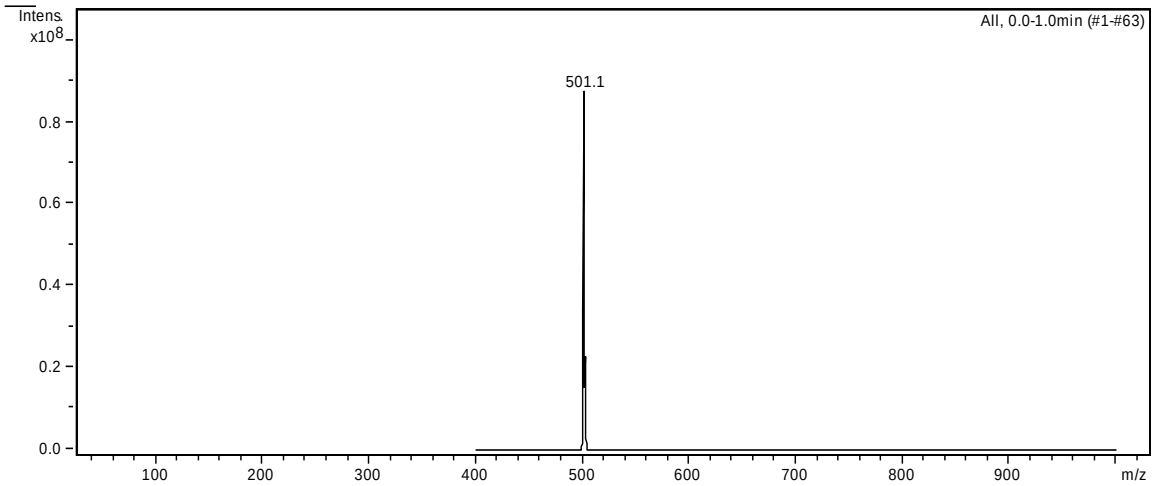

Fig. S20 ESI mass spectrum of cb-do2nph in H_2O/MeOH (9:2).