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Supporting Information

Mononuclear Bis(dithiolene) Mo(IV) and W(IV) Complexes with P, P; S, S; O, S and O, O Donor Ligands: A Comparative Reactivity Study

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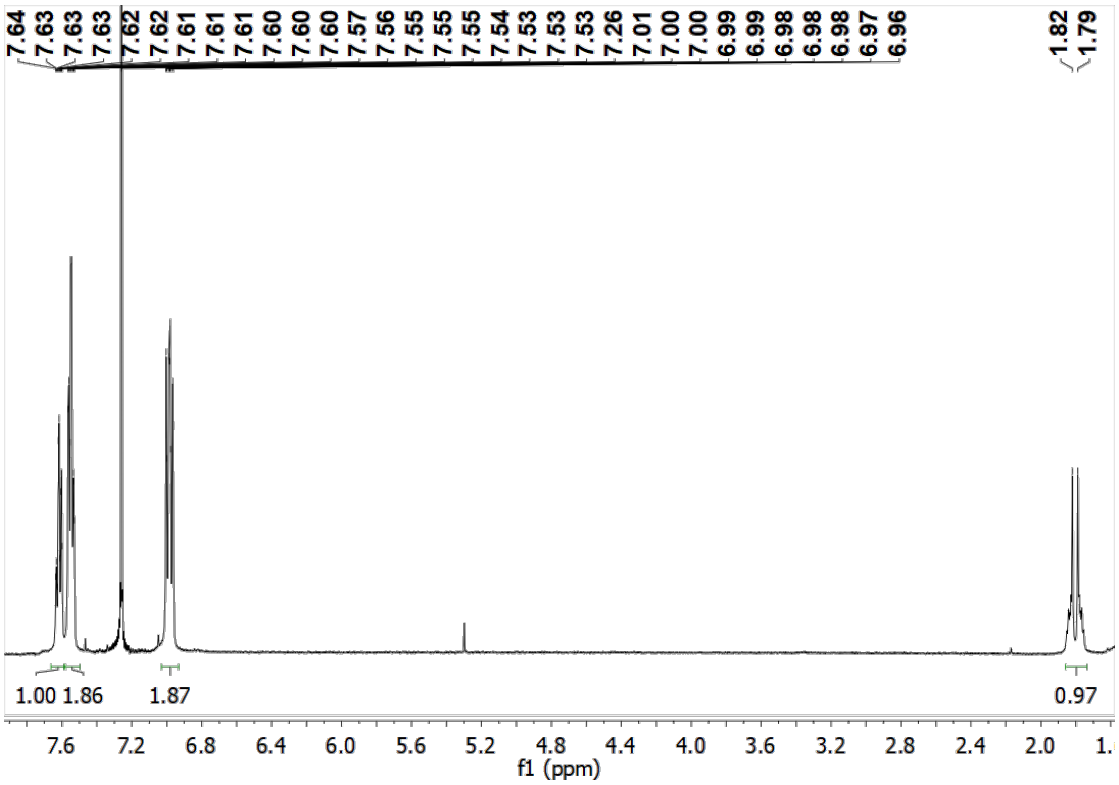


Fig. S1 ^{1}H NMR of **1a** in $CDCl_3$.

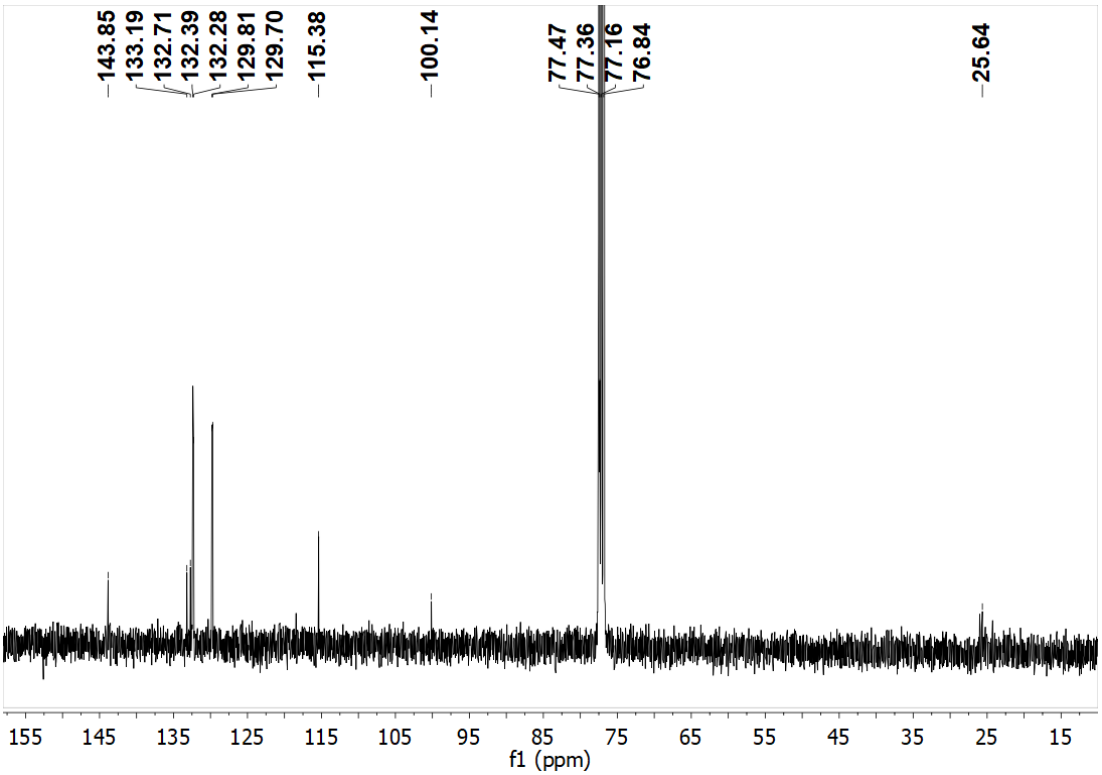


Fig. S2 ^{13}C NMR of **1a** in $CDCl_3$.

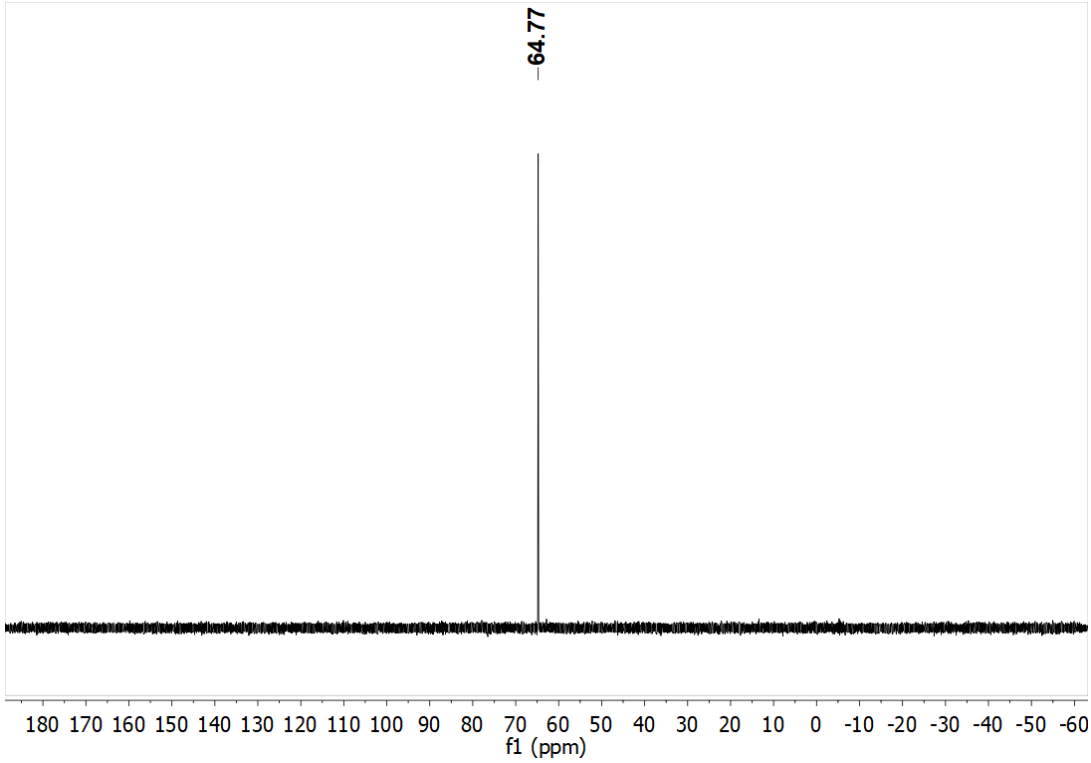


Fig. S3 ^{31}P NMR of **1a** in $CDCl_3$.

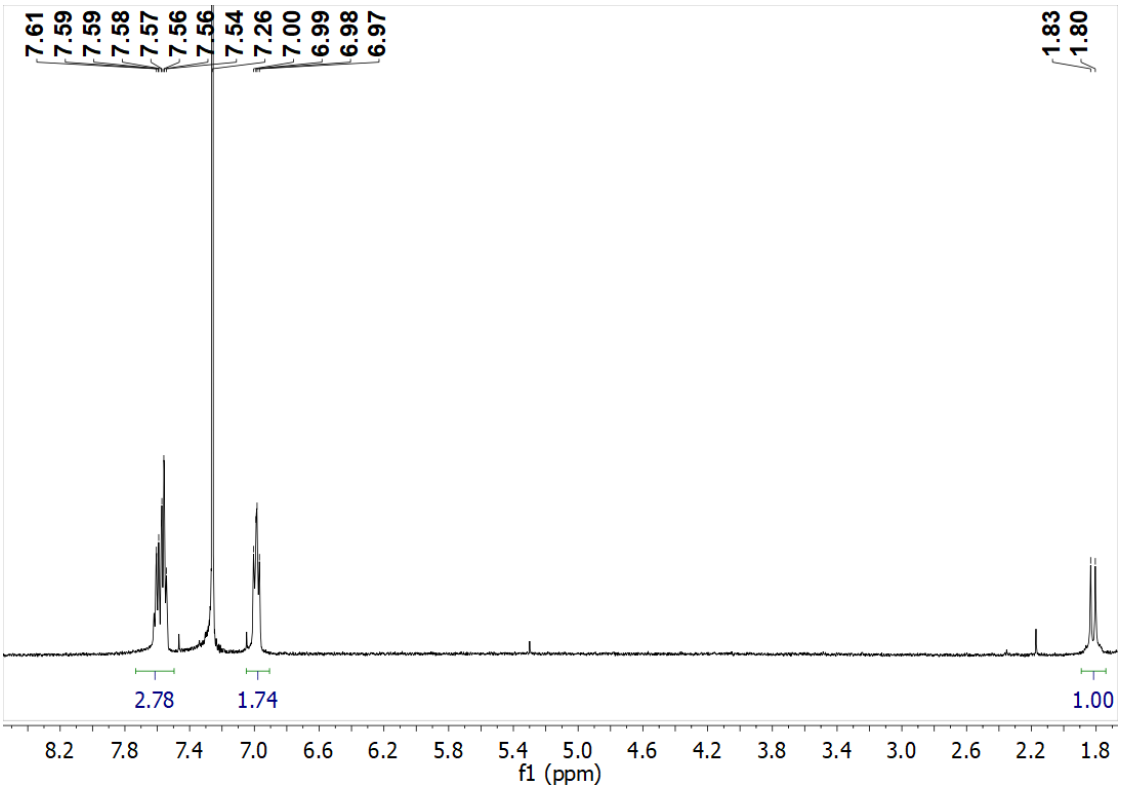


Fig. S4 ^{1}H NMR of **1b** in $CDCl_3$.

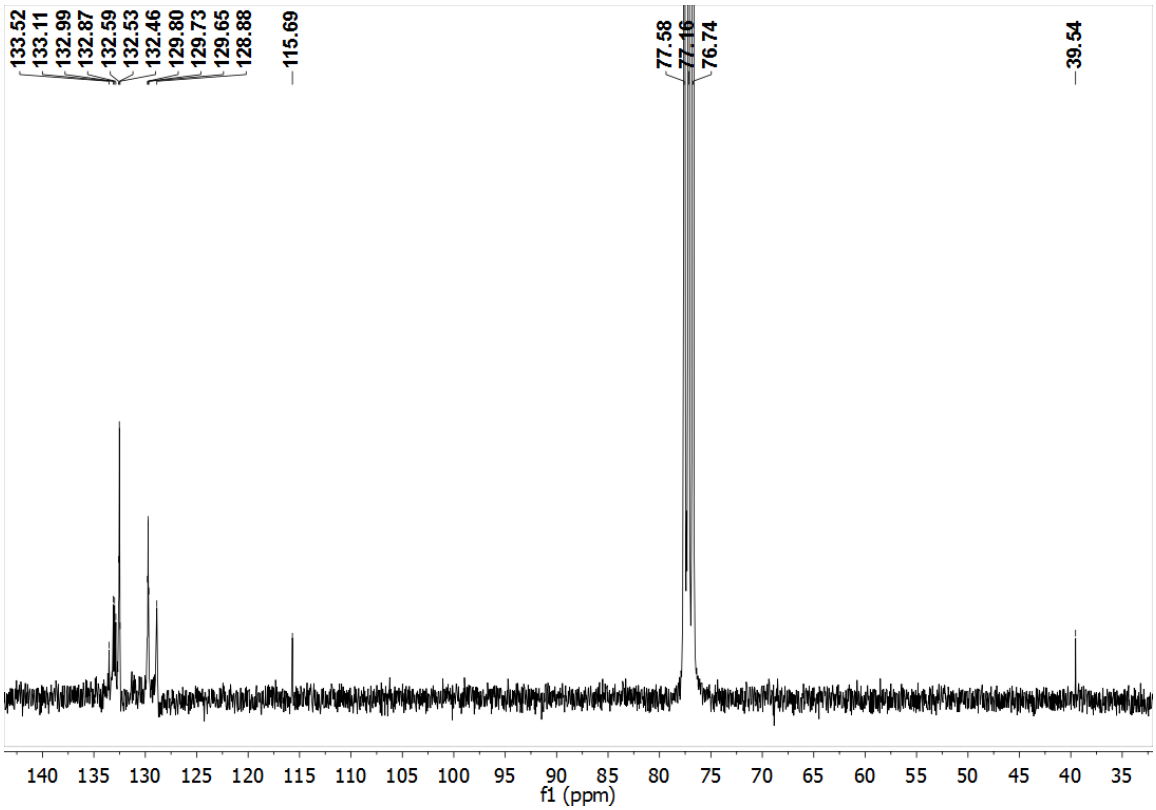


Fig. S5 ^{13}C NMR of **1b** in $CDCl_3$.

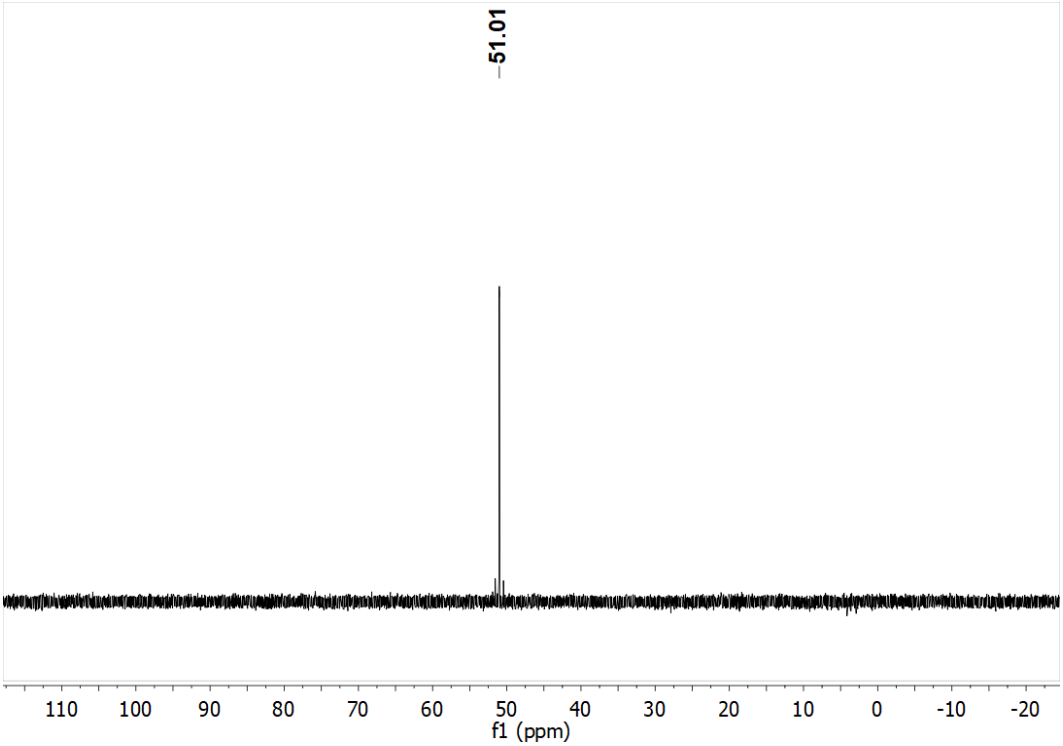


Fig. S6 ^{31}P NMR of **1b** in $CDCl_3$.

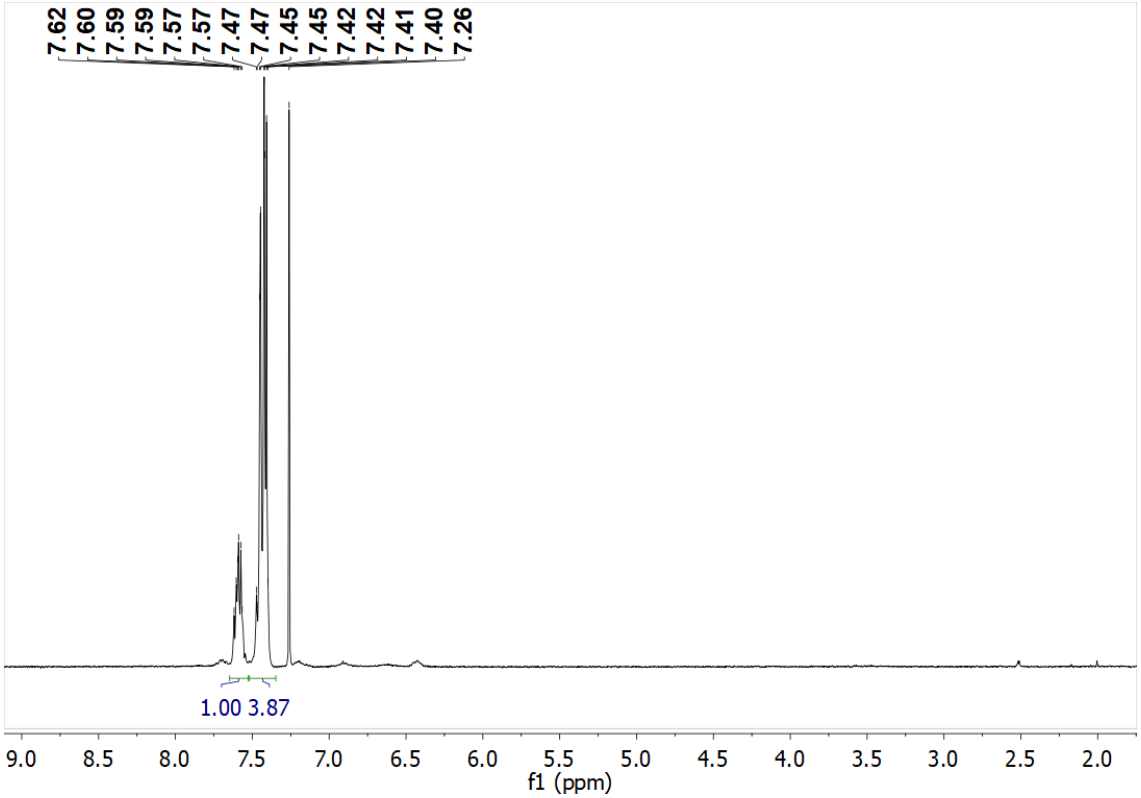


Fig. S7 ^{1}H NMR of **2a** in $CDCl_3$.

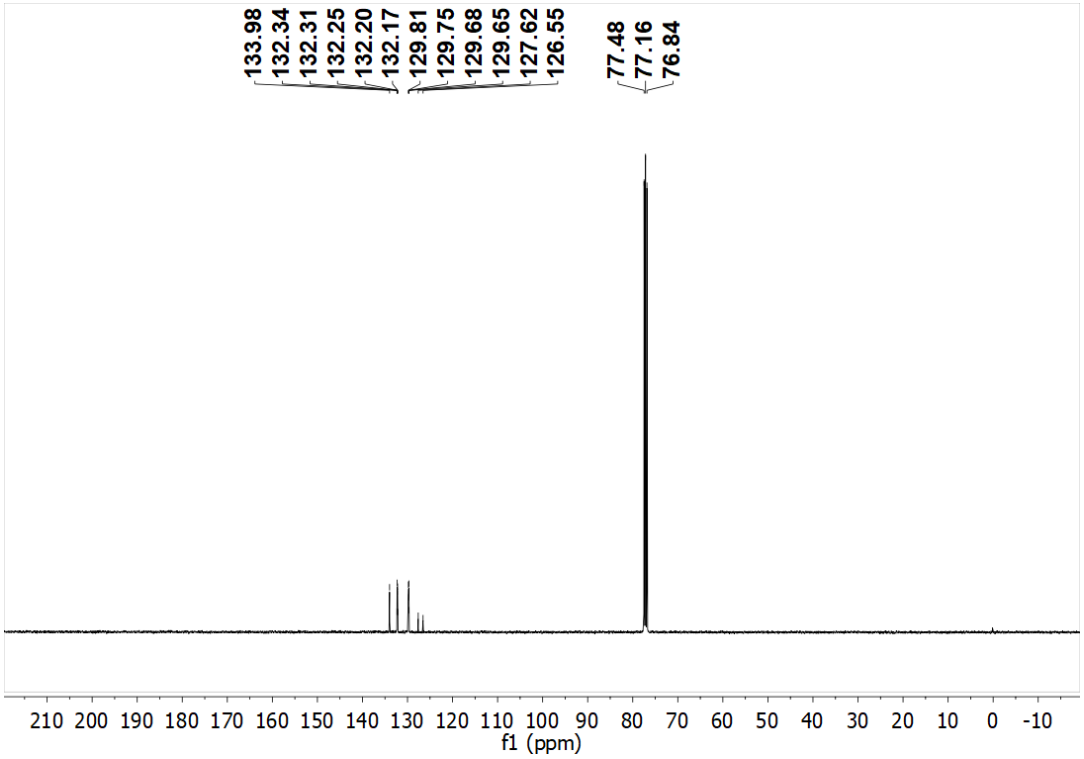


Fig. S8 ^{13}C NMR of **2a** in $CDCl_3$.

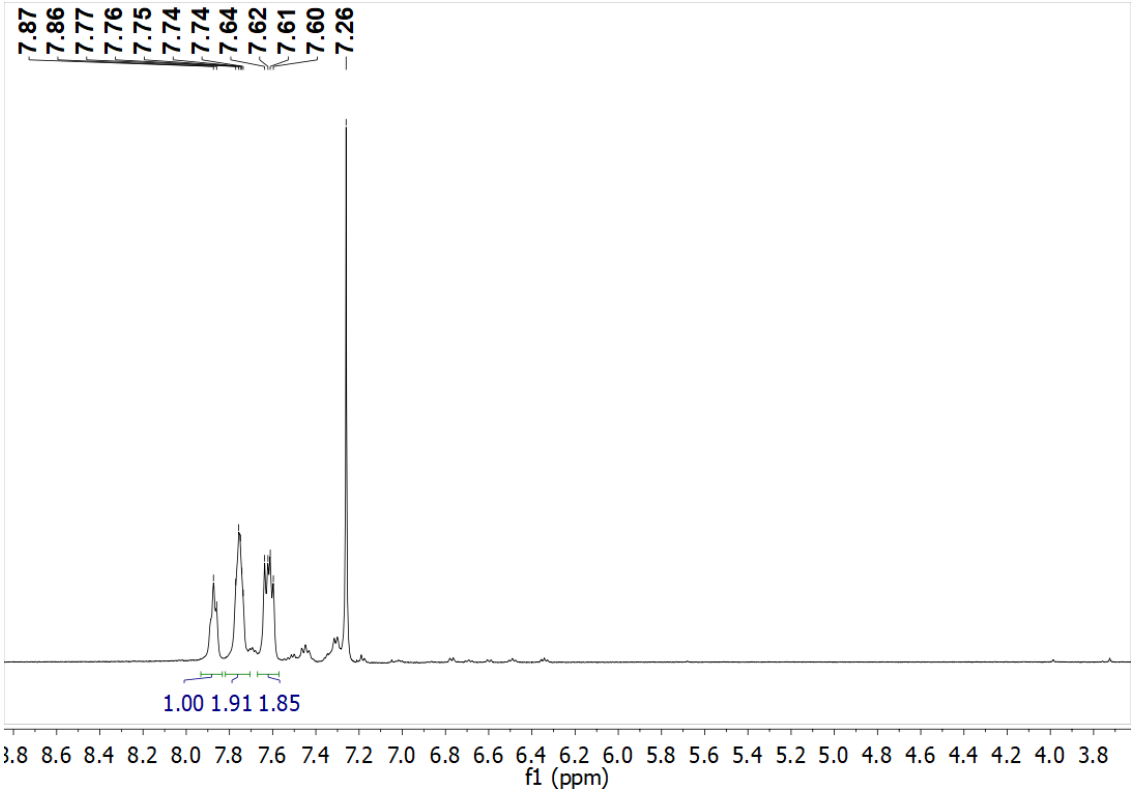


Fig. S9 ^{1}H NMR of **2b** in $CDCl_3$.

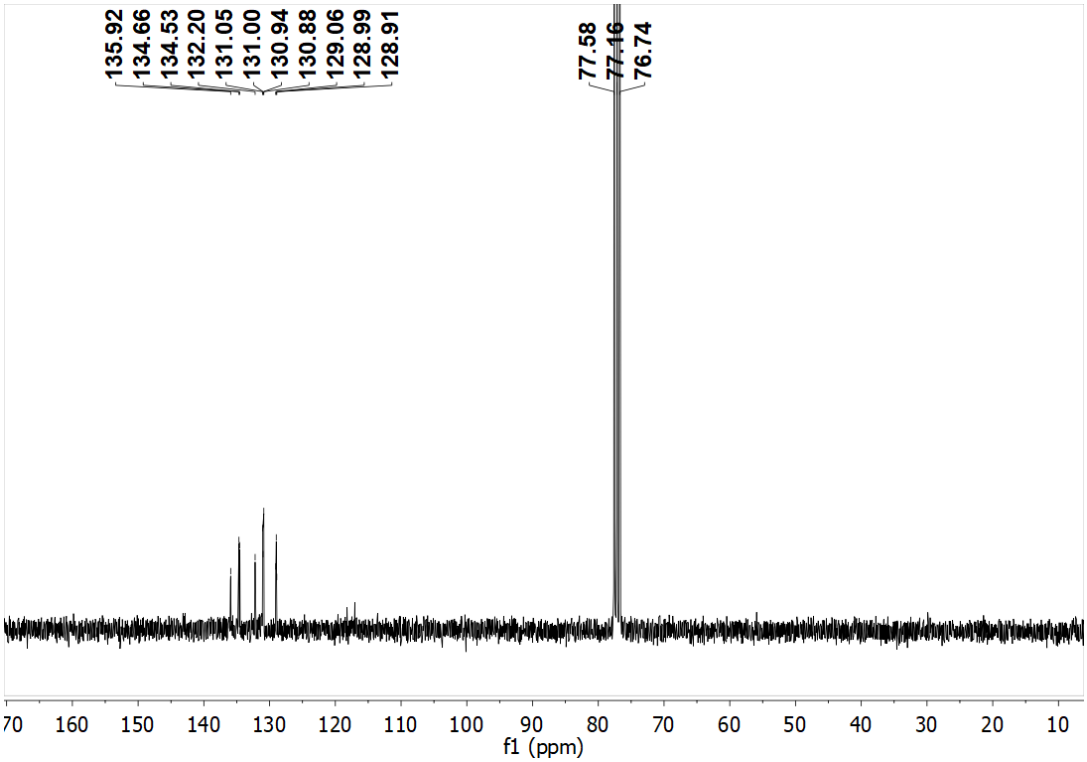


Fig. S10 ^{13}C NMR of **2b** in $CDCl_3$.

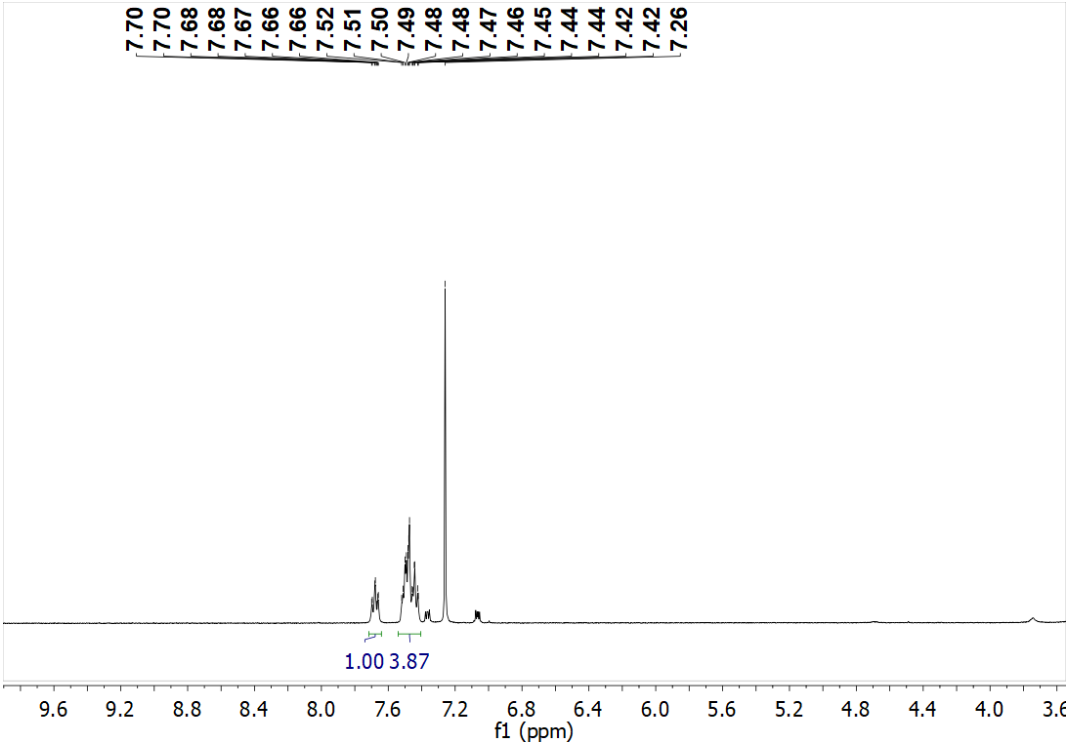


Fig. S11 ^{1}H NMR of **3a** in $CDCl_3$.

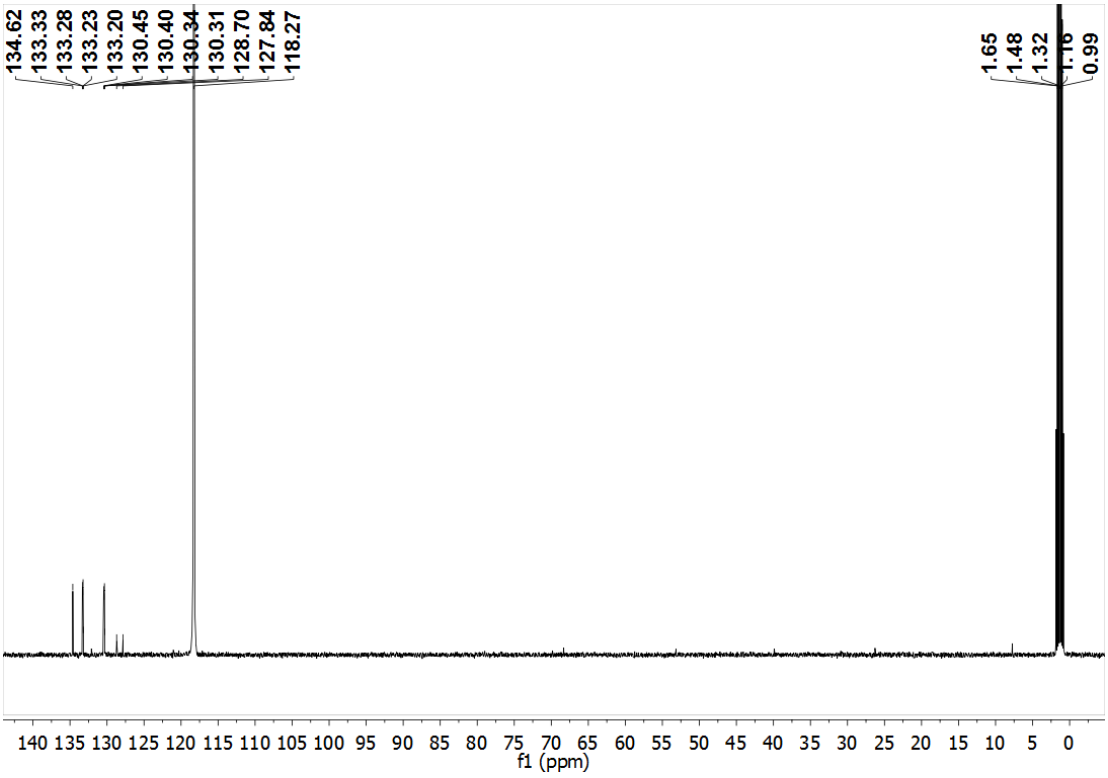


Fig. S12 ^{13}C NMR of **3a** in CD_3CN.

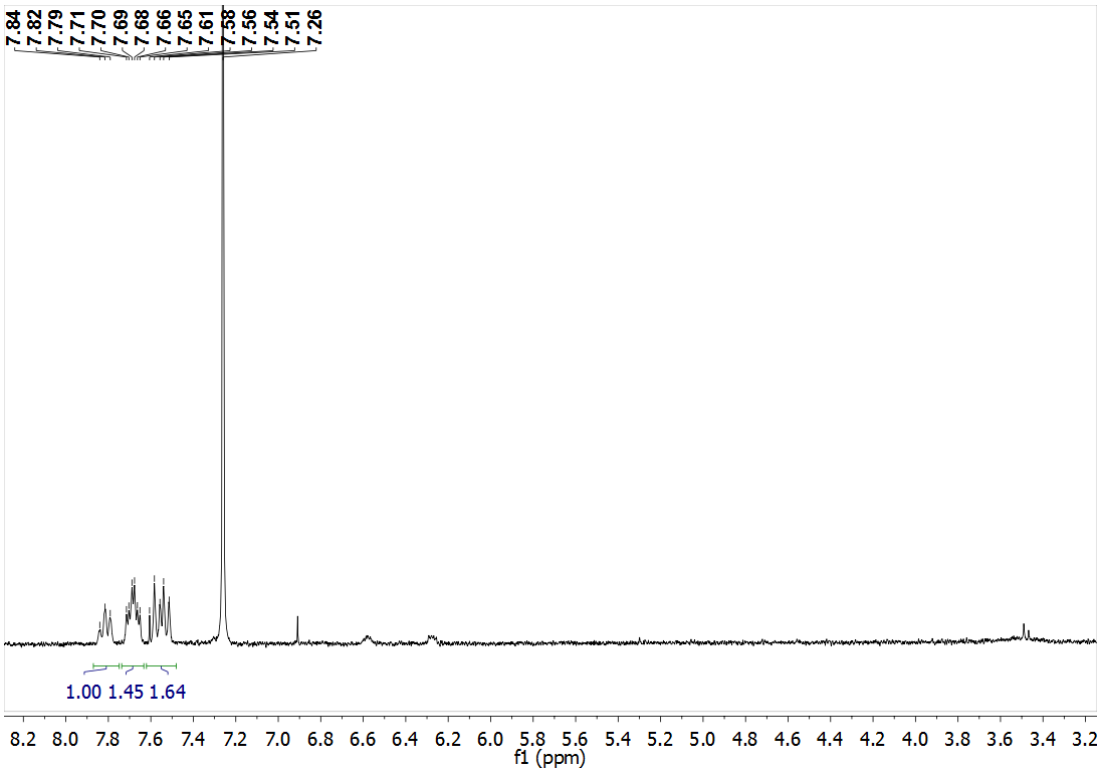


Fig. S13 ^{1}H NMR of **3b** in $CDCl_3$.

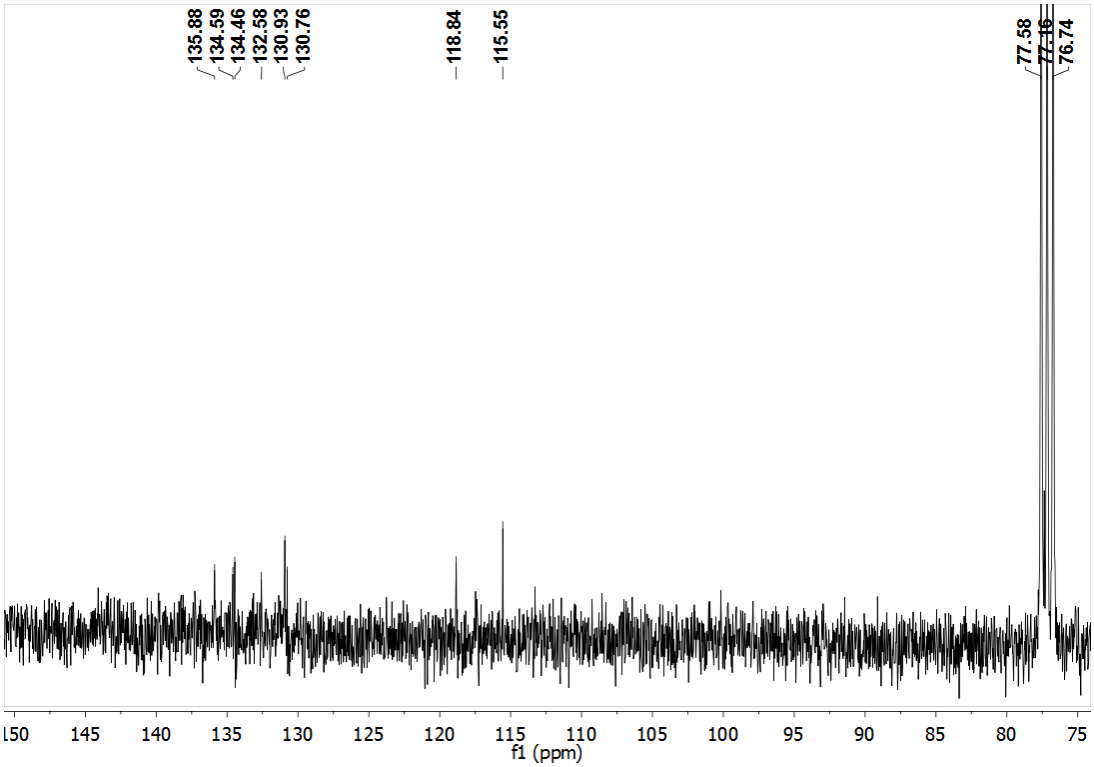


Fig. S14 ^{13}C NMR of **3b** in $CDCl_3$.

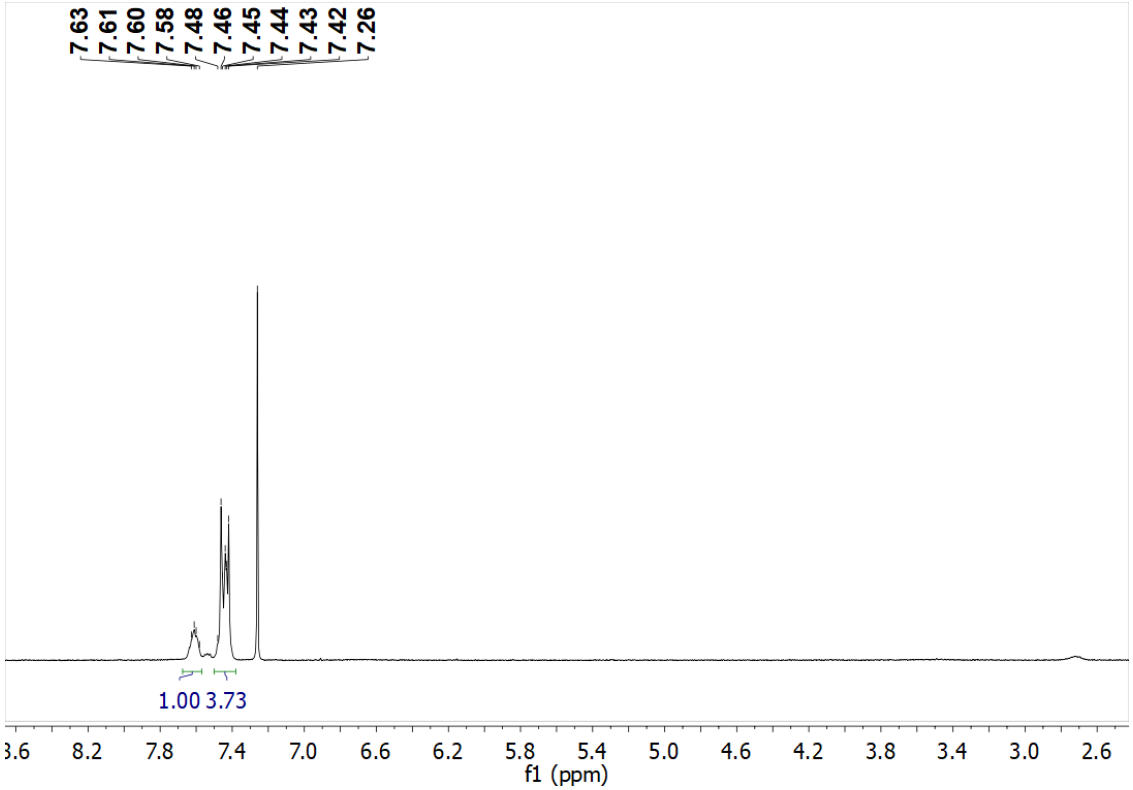


Fig. S15 ^{1}H NMR of **4a** in $CDCl_3$.

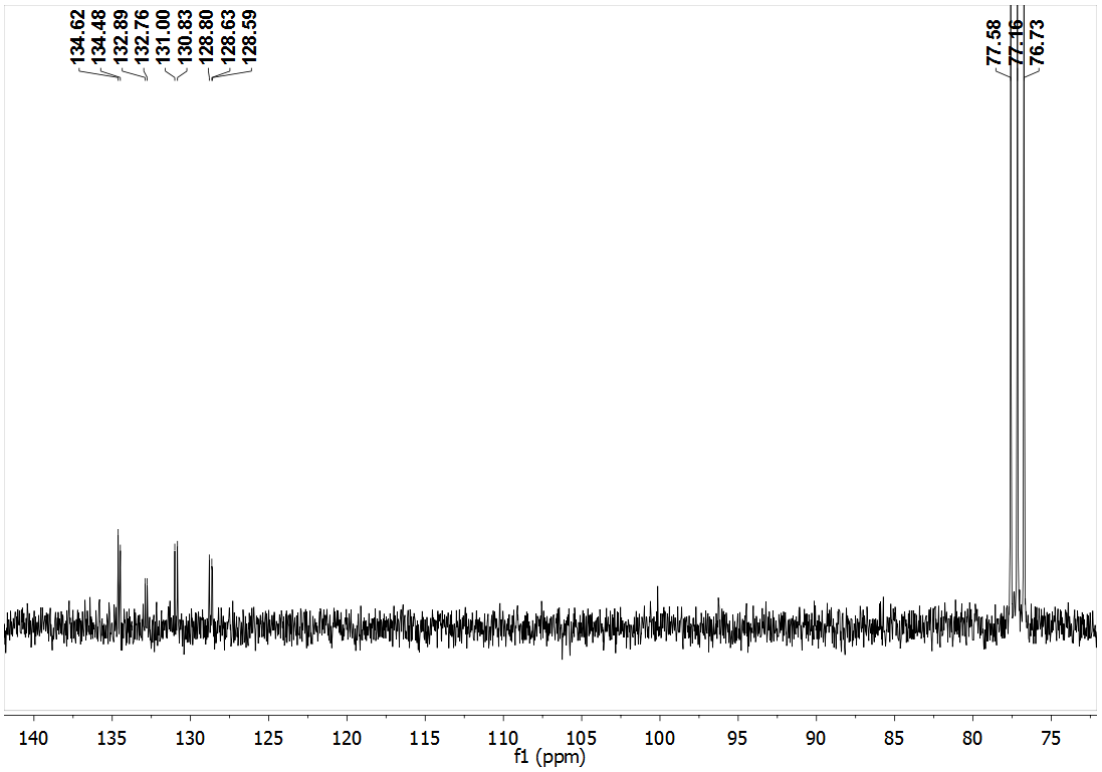


Fig. S16 ^{13}C NMR of **4a** in $CDCl_3$.

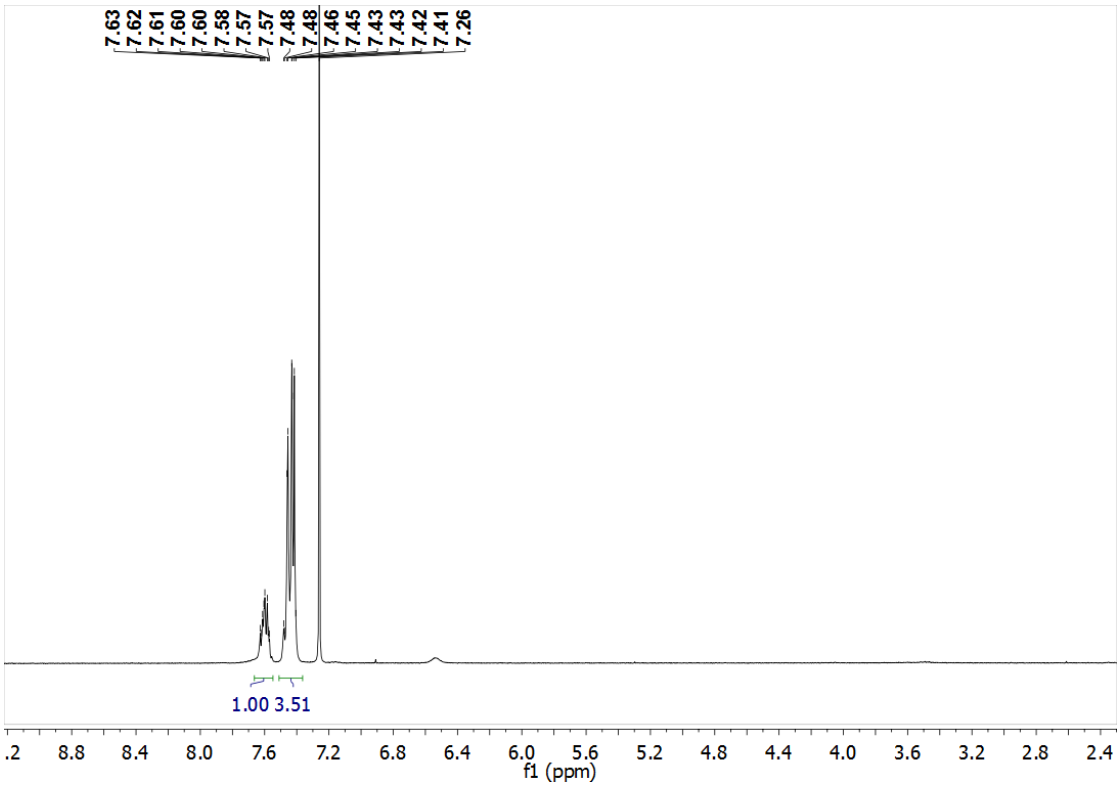


Fig. S17 ^{1}H NMR of **4b** in $CDCl_3$.

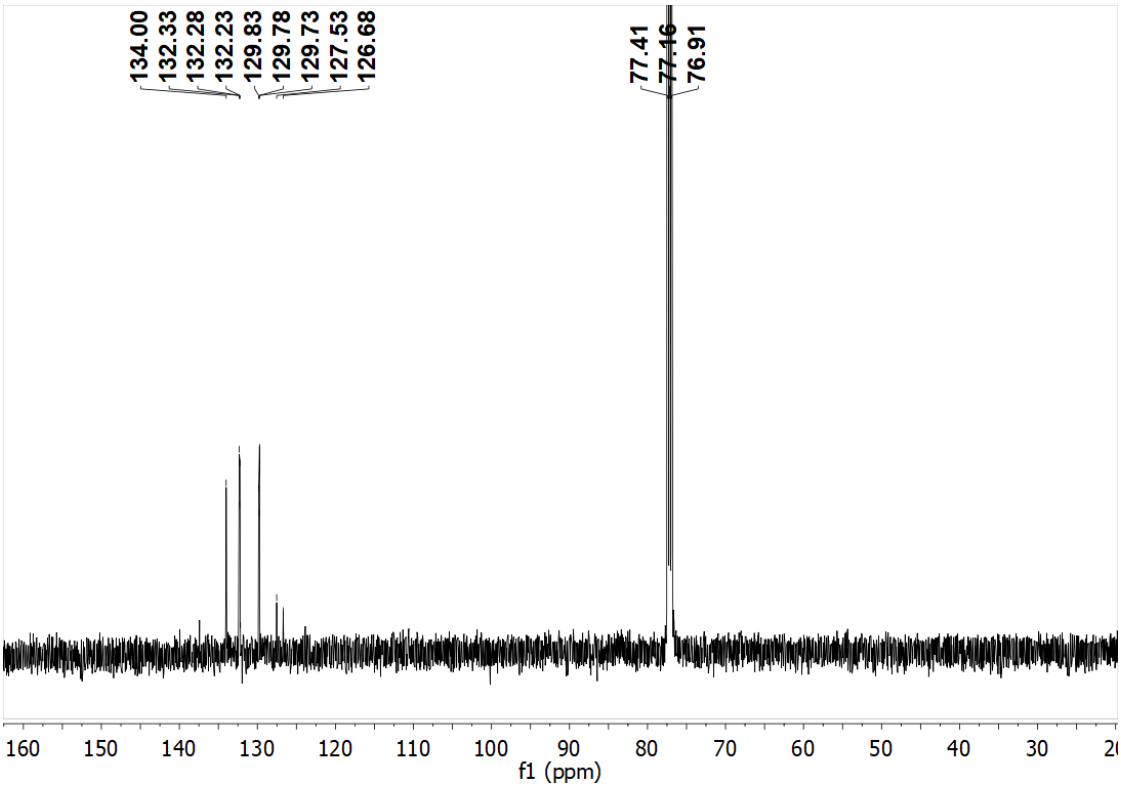


Fig. S18 ^{13}C NMR of **4b** in $CDCl_3$.

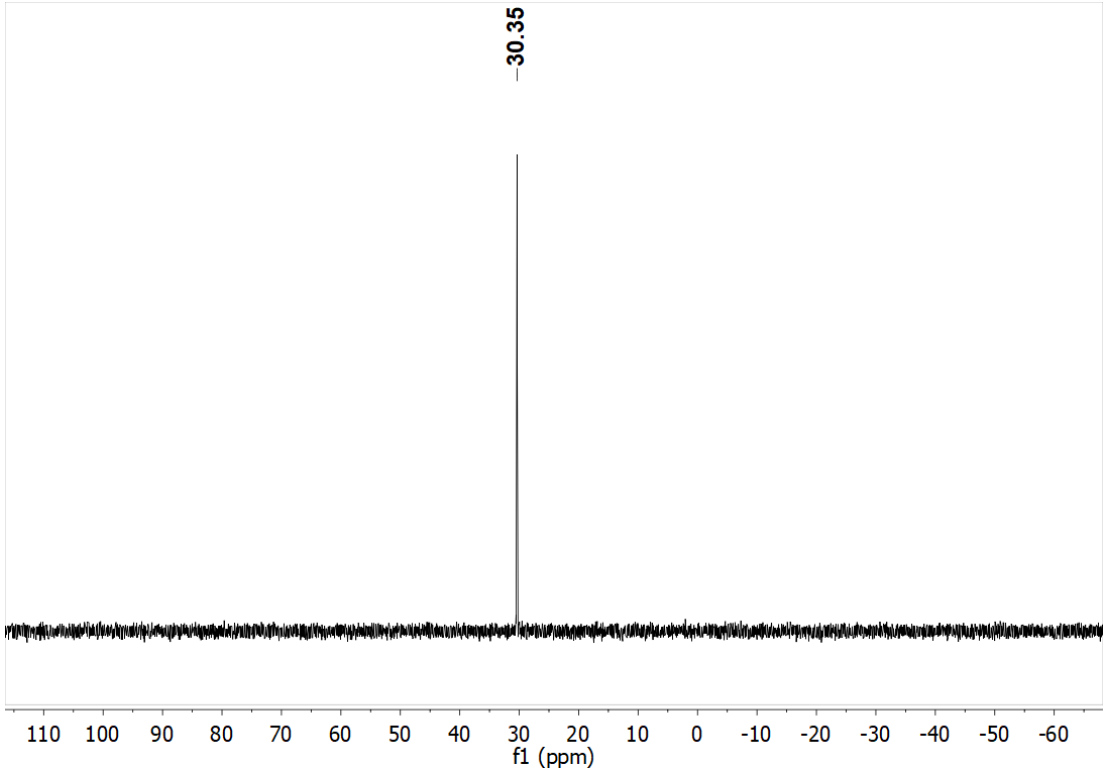


Fig. S19 ^{31}P NMR of **1a** + TMANO (1:2) in DMSO-d6.

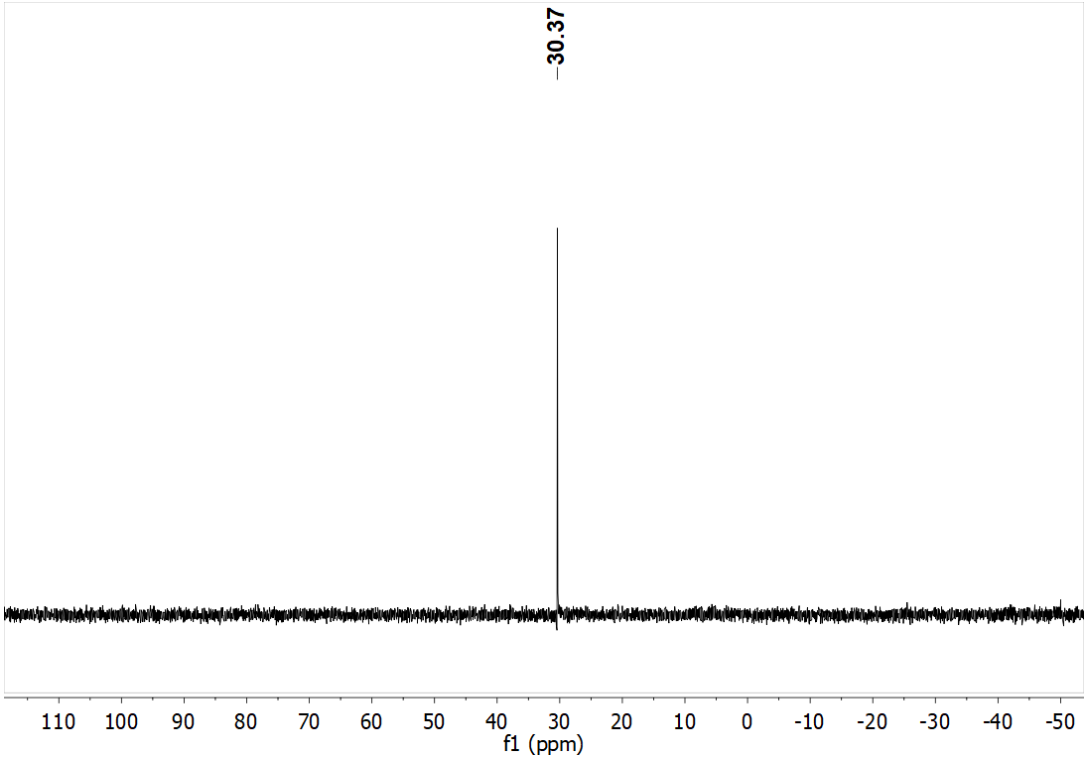


Fig. S 20 ^{31}P NMR of **1b** + TMANO (1:2) in DMSO-d6.

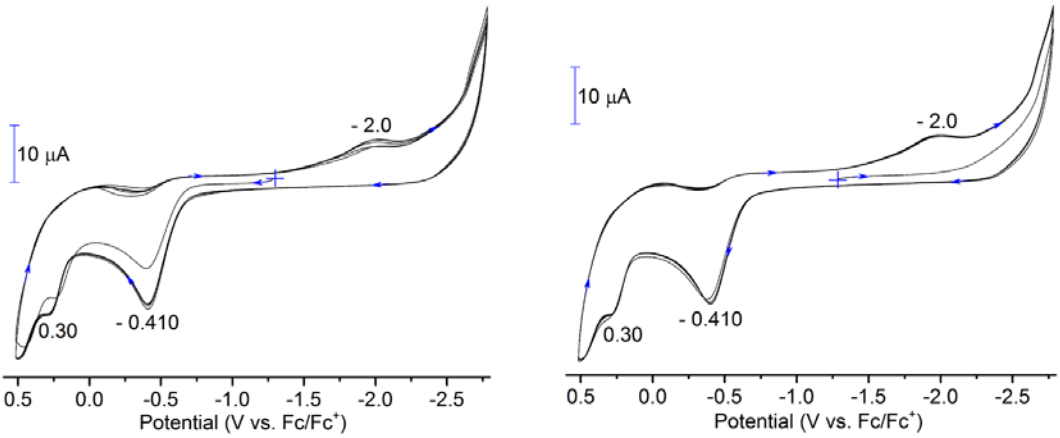


Fig. S21 Cyclic voltammetric traces (multiple scans, scan rate = 100 mV s^{-1}) for Na_2mnt in MeCN.

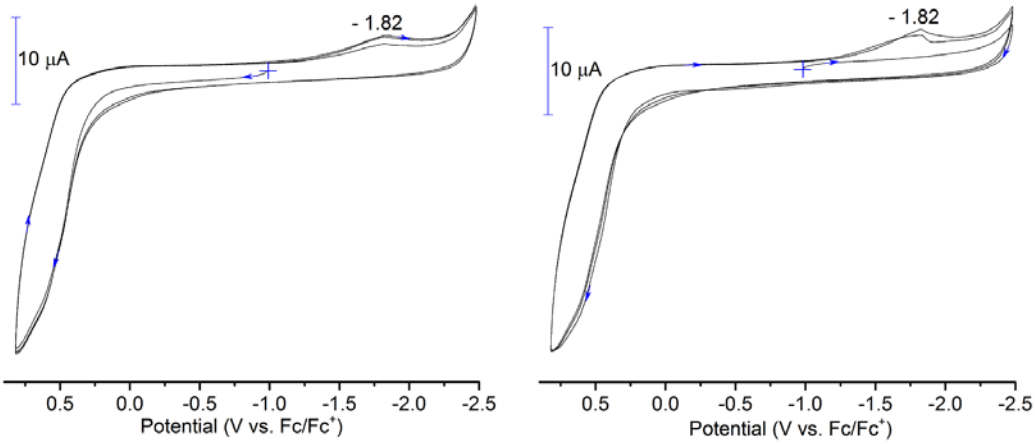


Fig. S22 Cyclic voltammetric traces (multiple scans, scan rate = 100 mV s^{-1}) for dppe in MeCN.

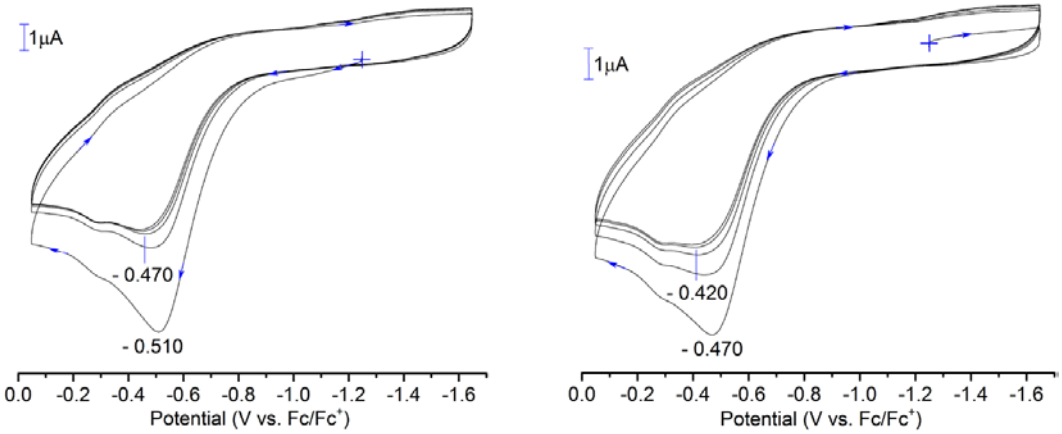


Fig. S23 Cyclic voltammetric traces (multiple scans, scan rate = 100 mV s^{-1}) for Li_2bdt in DMF.

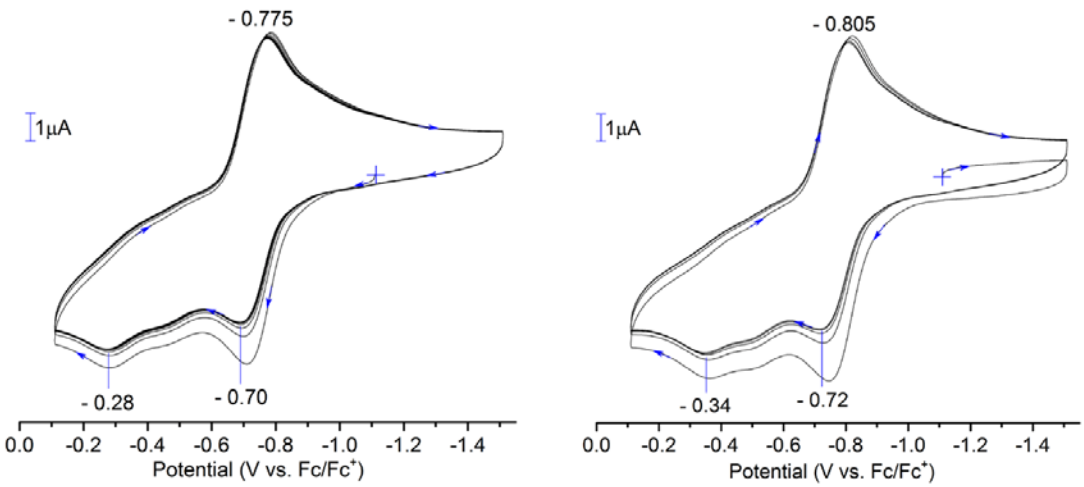


Fig. S24 Cyclic voltammetric traces (multiple scans, scan rate = 100 mV s^{-1}) for Na_2(catecholate) in DMF.

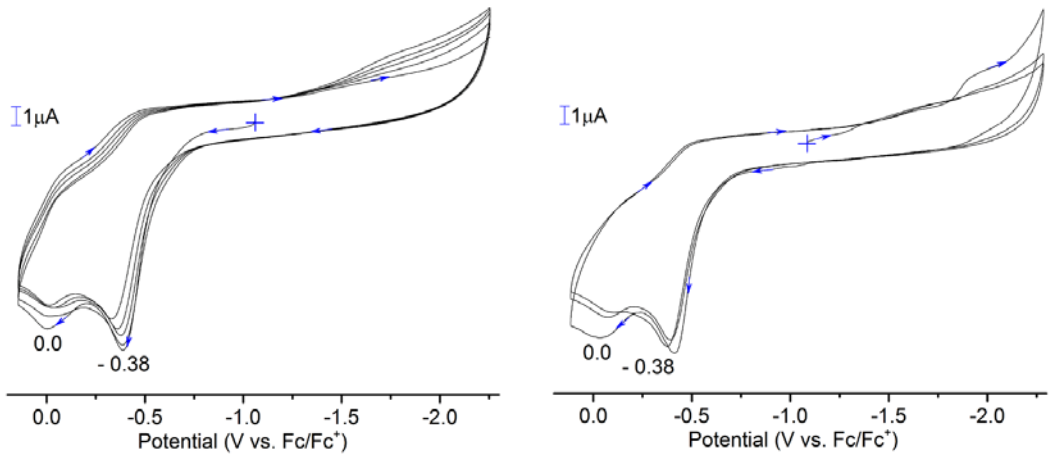
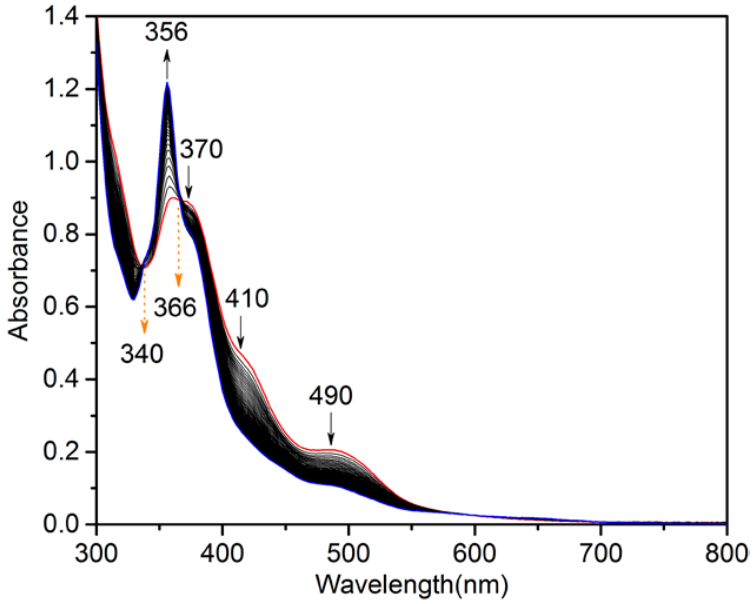
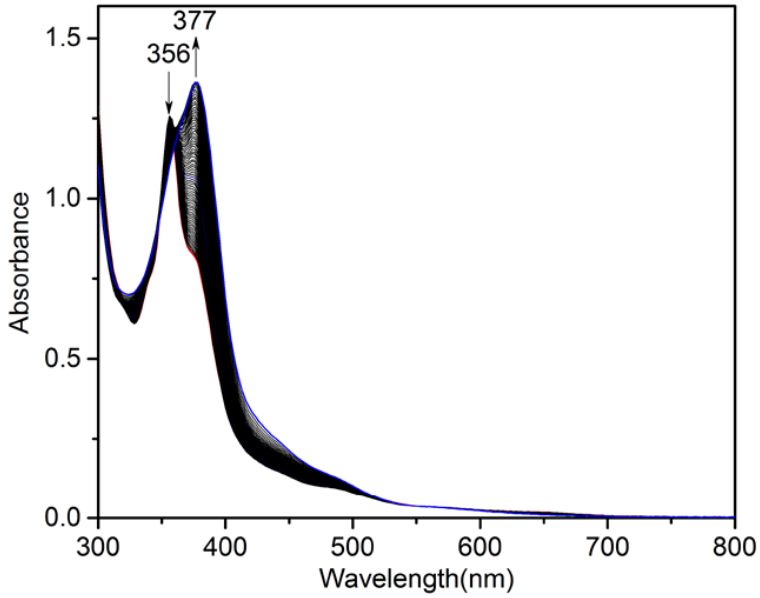


Fig. S25 Cyclic voltammetric traces (multiple scans, scan rate = 100 mV s^{-1}) for Na_2(2-mercaptophenolate) in DMF.



(a)



(b)

Fig. S26 Absorption spectroscopic monitoring for the reaction of **1b** with TMANO in MeCN in the presence of AcOH. [**1b**] = 0.1 mM; [TMANO] = 0.35 mM. (a) First stage of reaction indicates conversion of **1b** to $[WO(mnt)_2]^{2-}$; scan interval = 1 min total time = 50 min.; red line: initial scan within 30 seconds of mixing; blue line: spectrum after 50 min. (b) Second stage of reaction indicates partial conversion of insitu generated $[WO(mnt)_2]^{2-}$ to $[WO_2(mnt)_2]^{2-}$; scan interval = 5 min total time = 6.5 h. red line: initial scan within 30 seconds of mixing; blue line: spectrum after 6.5 h.