Equation Supplementary Information

$$2\ [PdBr(P_3)]Br + 2\ H_2O_2 \xrightarrow[(2\ /\ 1)]{Me_2CO\ /\ Et_2O} [Pd(P_2PO)_2][PdBr_4] + 2\ H_2O \quad (S1)$$

Scheme and Figure Captions. Supplementary Information

Scheme S1. Proposed equilibria involving five- and four-coordinate species for oxidations of **1-6** with H_2O_2.

Scheme S2. Proposed equilibria for reactions of **3** and **6** in DMSO-d_6 wit GSH in D_2O.

Scheme S3. Trigonal-bipyramidal and/or square-planar thiolates obtained from $[PtI(NP_3)]I$ in DMSO-d_6 and $[PdCl(NP_3)]Cl$ in CD_3OD by addition of GSH in D_2O.

Figure S1. ORTEP diagram for **13∗** . 50% probability of thermal ellipsoid drawn and solvents removed for clarity.

Figure S2. $^{31}P\{^1H\}$NMR Spectra in $CDCl_3$ (r.t.) for **1** (top)**, 2** (middle) and **3** (bottom) and their products of reaction with 12 molar equivalents of H_2O_2.

Figure S3. $^{195}Pt\{^1H\}$NMR Spectrum (r.t.) of **10** in DMSO-d_6

Figure S4. Titration (r.t) of **10**·$2H_2O$ (bottom) with CuCl in $CDCl_3$ followed by $^{31}P\{^1H\}$NMR

Figure S5. $^{31}P\{^1H\}$NMR spectra for titration of **4** with 1-3 (bottom - top) equivalents of GSH in DMSO-d_6 + D_2O

Figure S6. $^{31}P\{^{1}H\}$NMR Spectrum (r.t.) for **1+3 eq.GSH** in DMSO-d_6+D_2O (pH= 4.0)

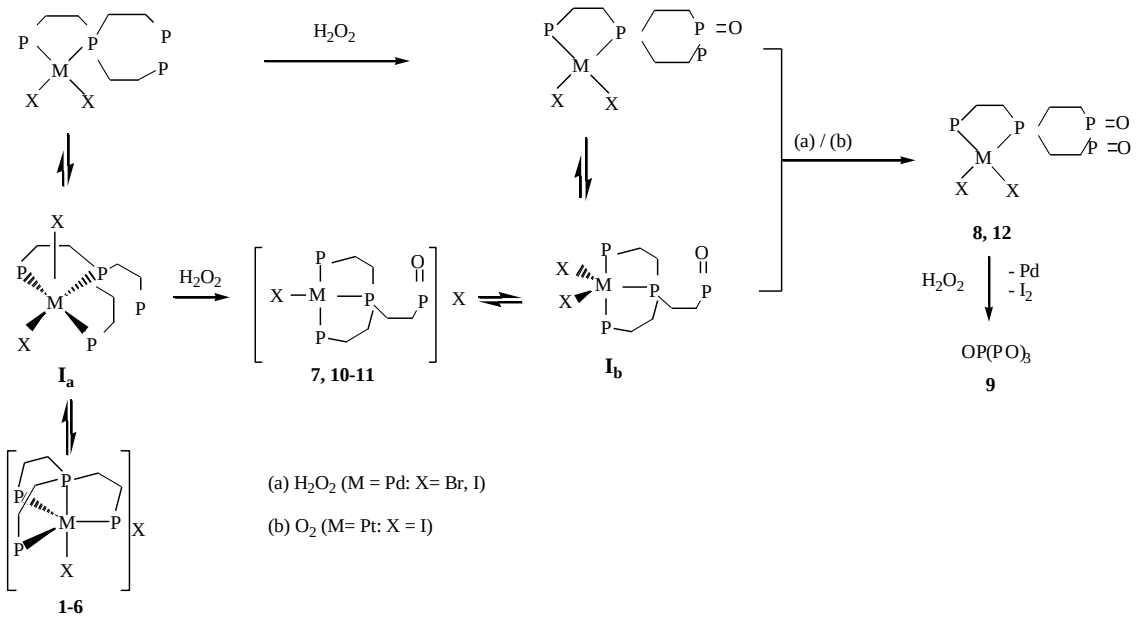
Figure S7. ^{1}HNMR Spectra (r.t.) in DMSO-d_6+D_2O for : **1+3eq. GSH** (top) and **4+ 3eq.GSH** (bottom)

Figure S8. $^{31}P\{^{1}H\}$NMR spectra (r.t.) for titration of **10** with 1-3 (bottom - top) equivalents of GSH in DMSO-d_6 + D_2O

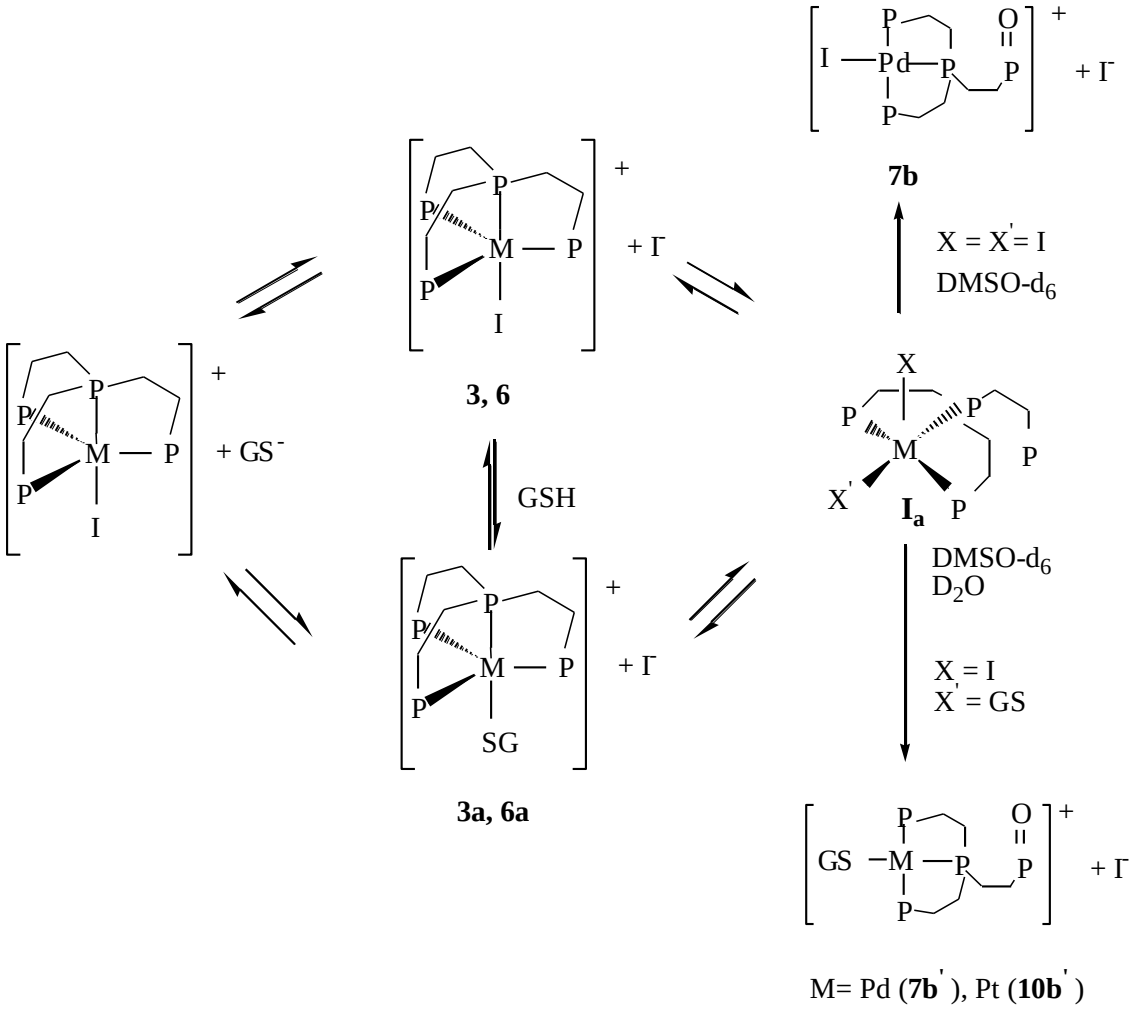
Figure S9. $^{31}P\{^{1}H\}$NMR spectra (r.t.) for : **3** in DMSO-d_6 (bottom) and the reactions with 1 (middle) and 2 (top) equivalents of GSH

Figure S10. Titration (r.t.) followed by $^{31}P\{^{1}H\}$NMR of [PdCl(NP_3)]Cl with GSH in CD_3OD/D_2O giving [Pd(SG)(NP_3)]Cl and [Pd(SG)(NP_2PO)]Cl

Scheme S1



Scheme S2



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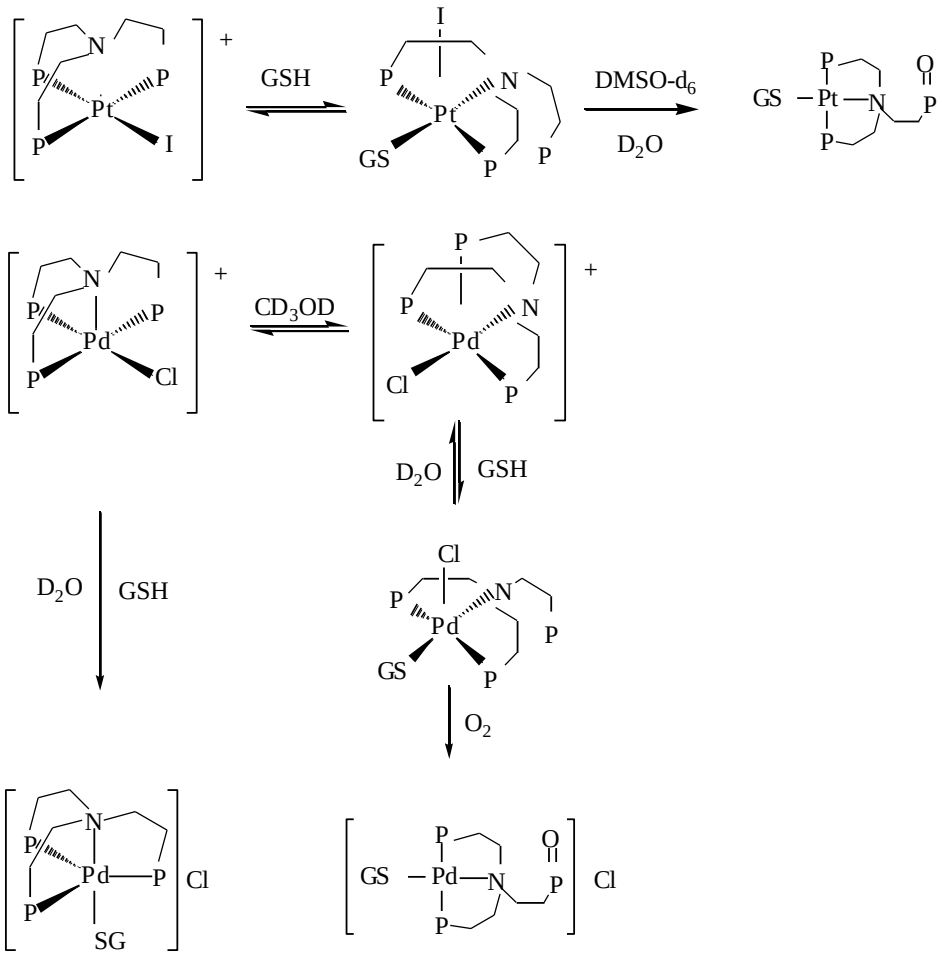


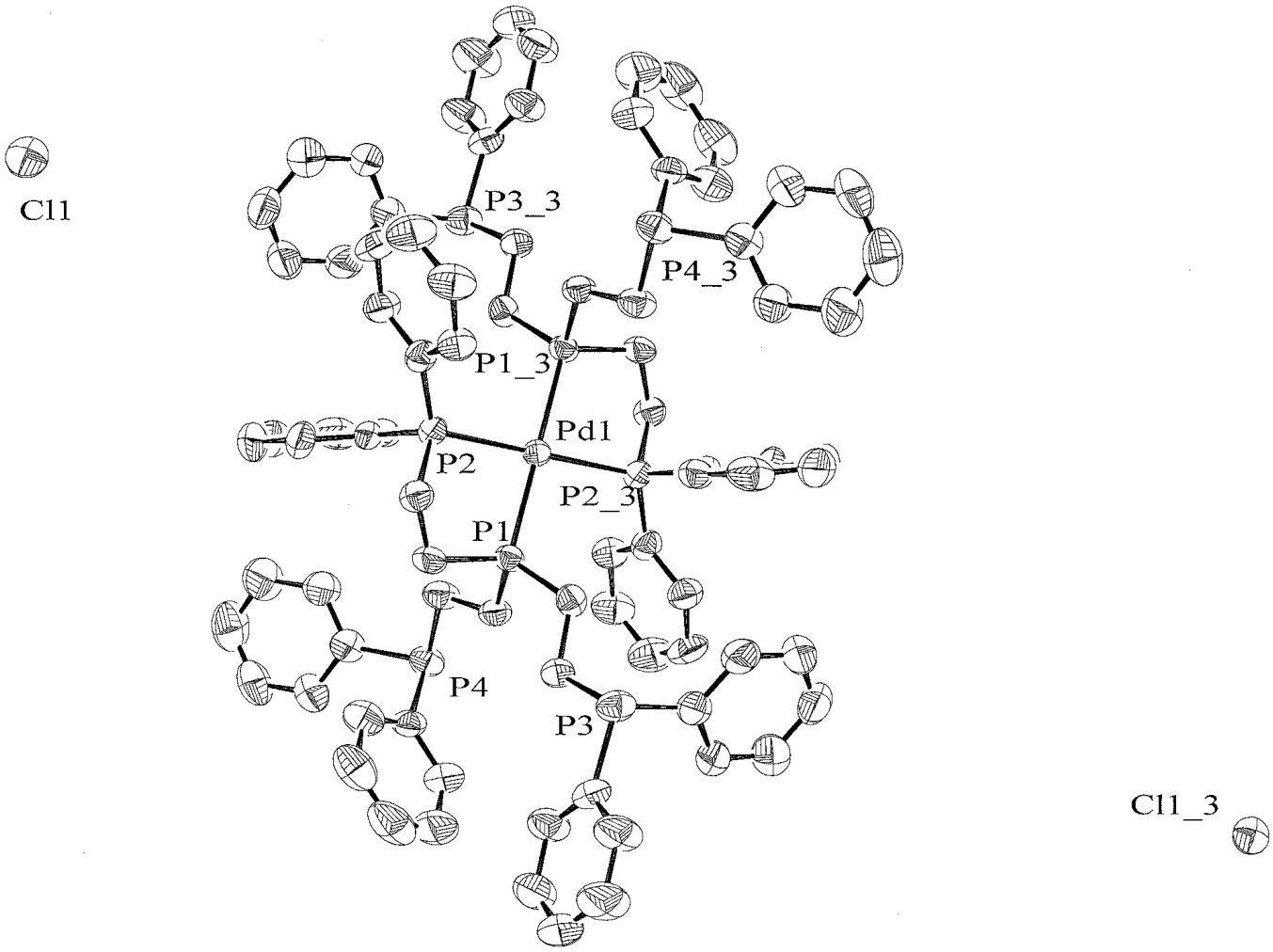


Figure S1

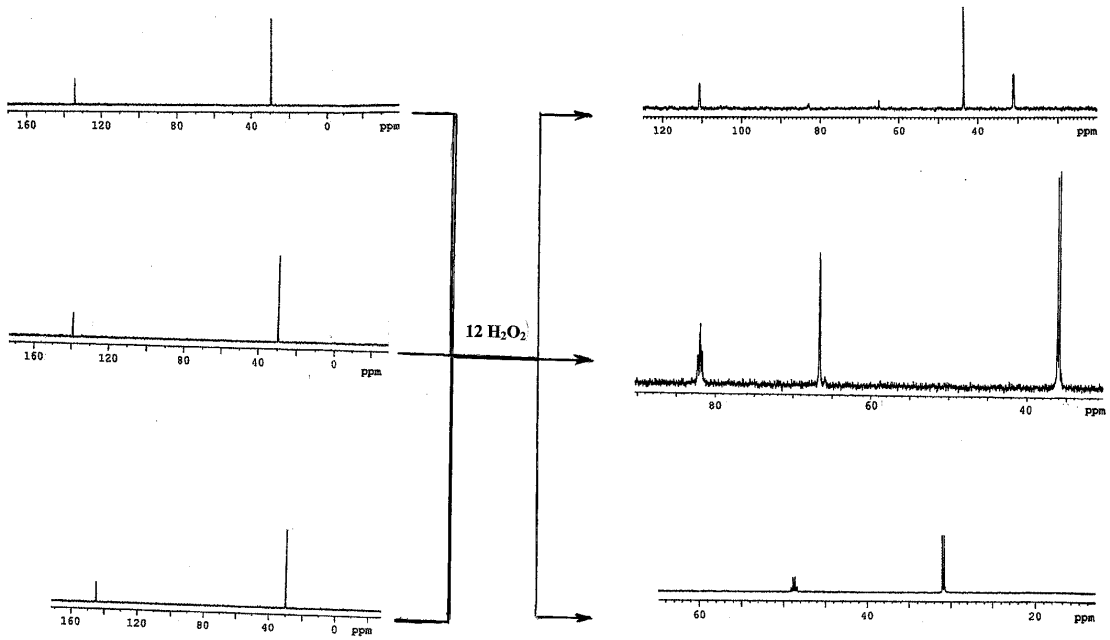


Figure S2

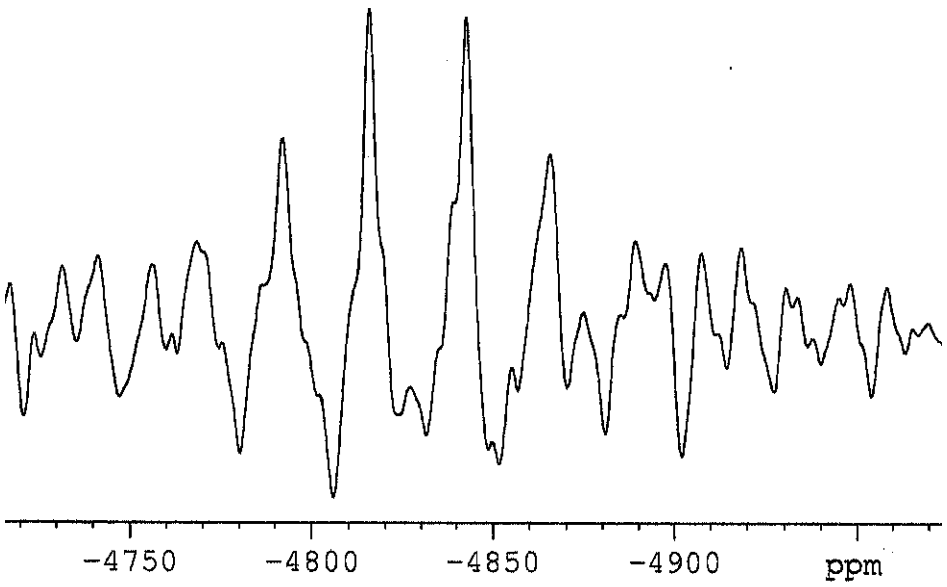


Figure S3

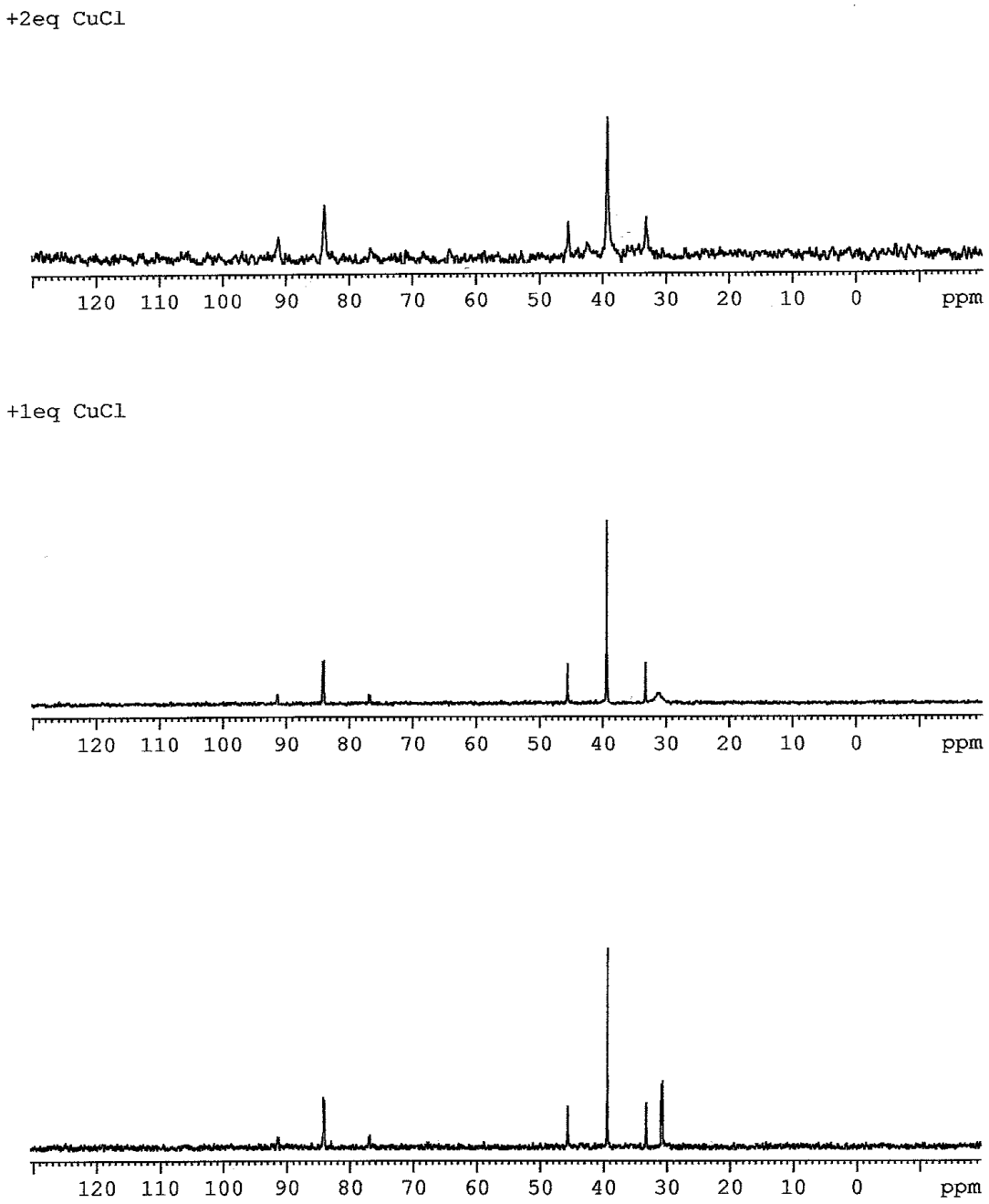


Figure S4

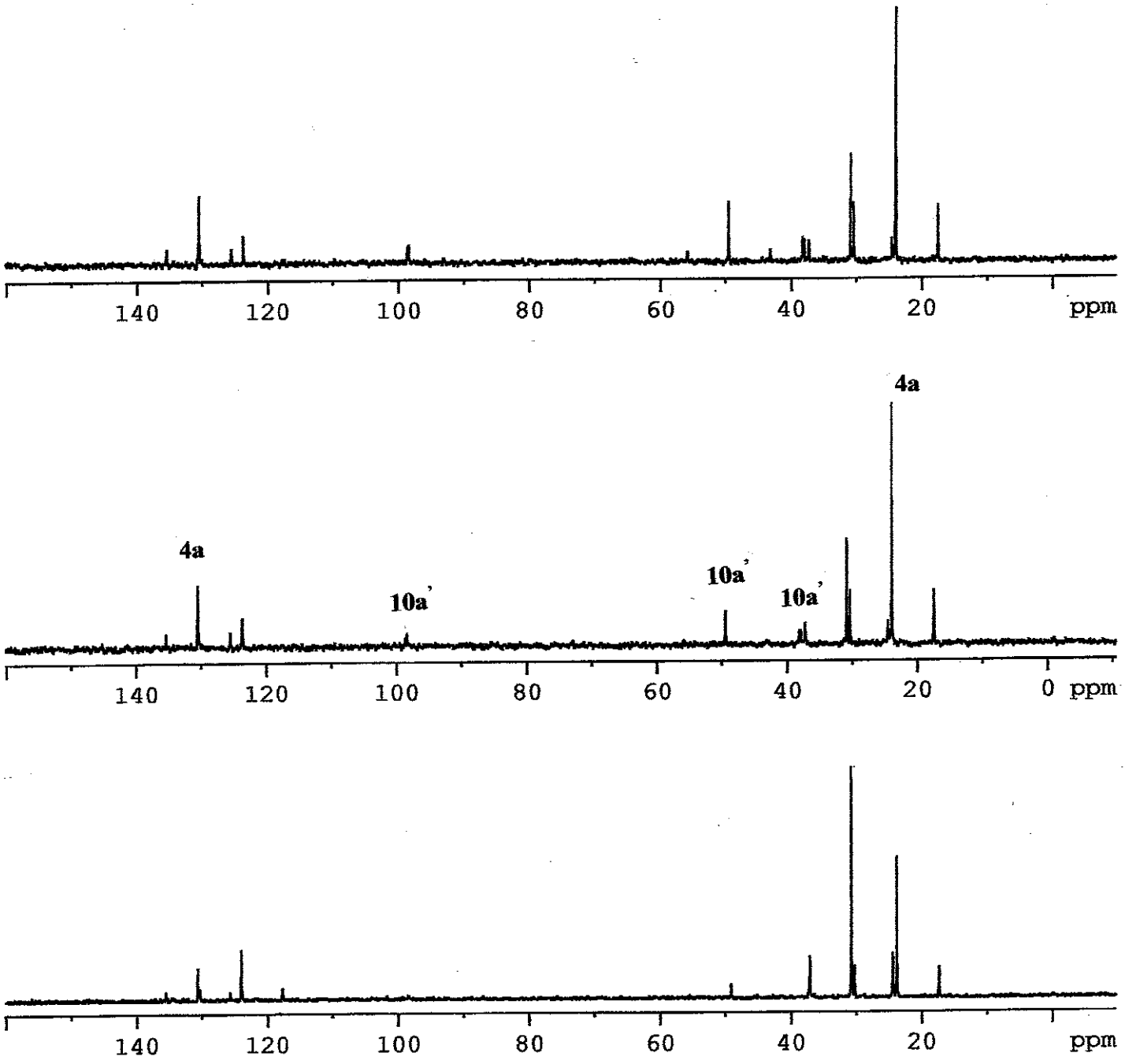


Figure S5

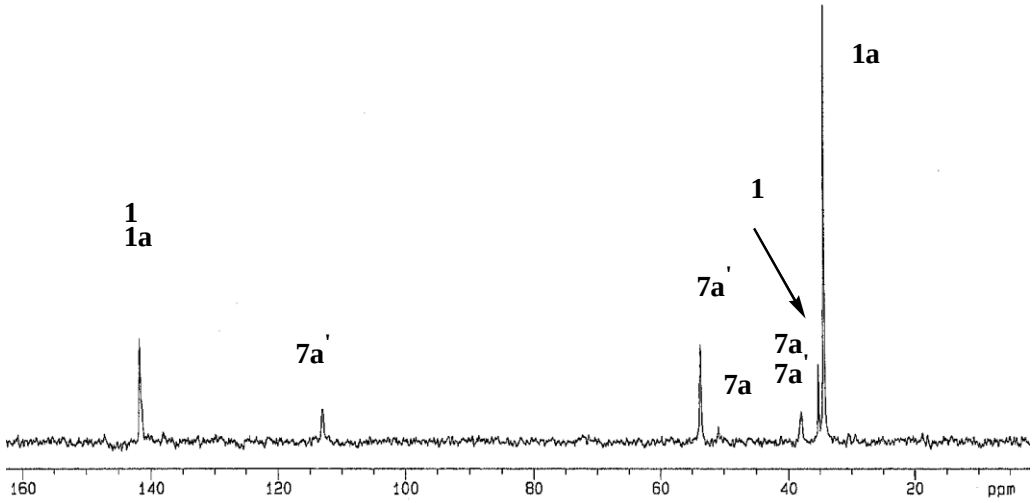


Figure S6

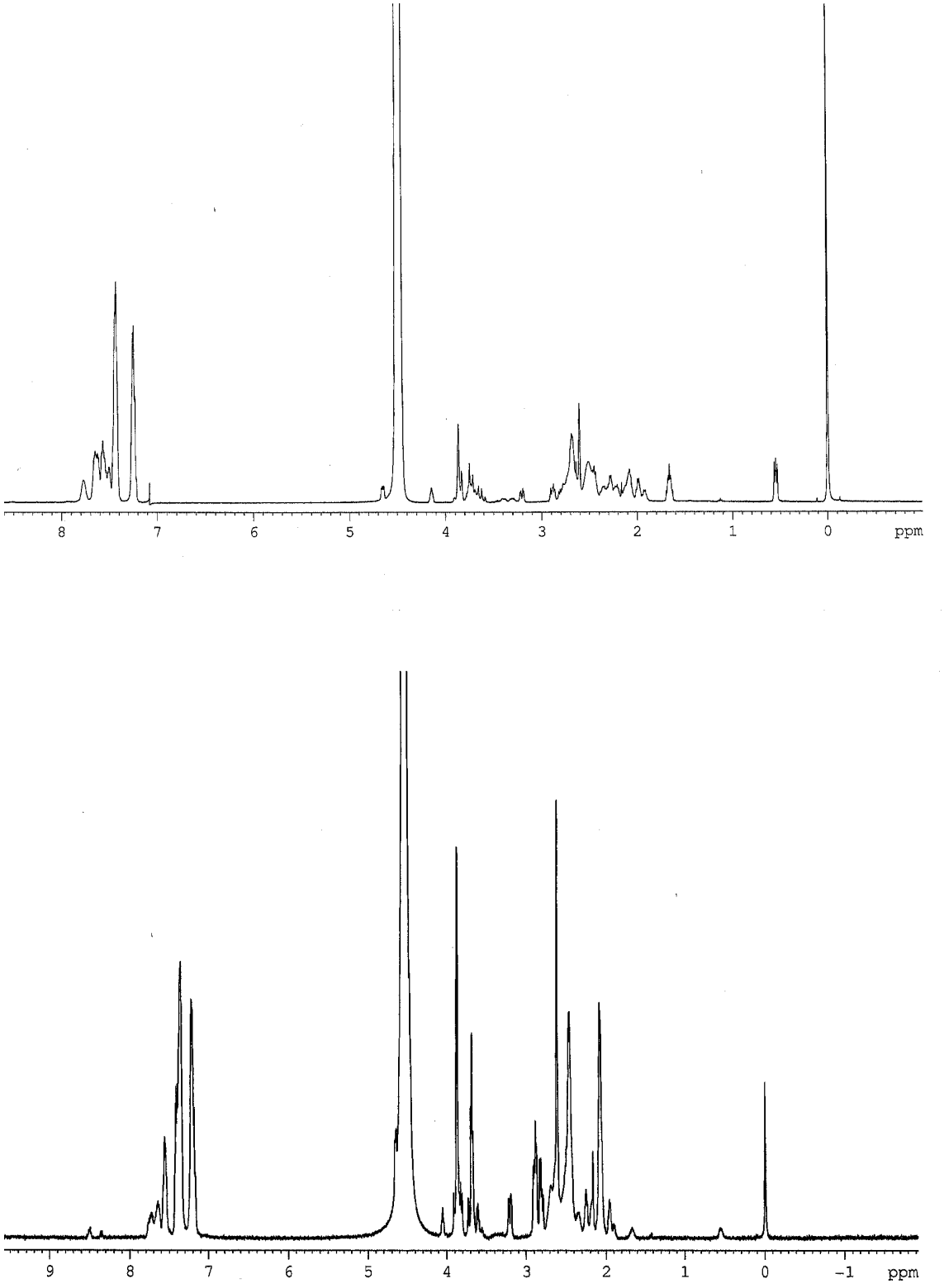


Figure S7

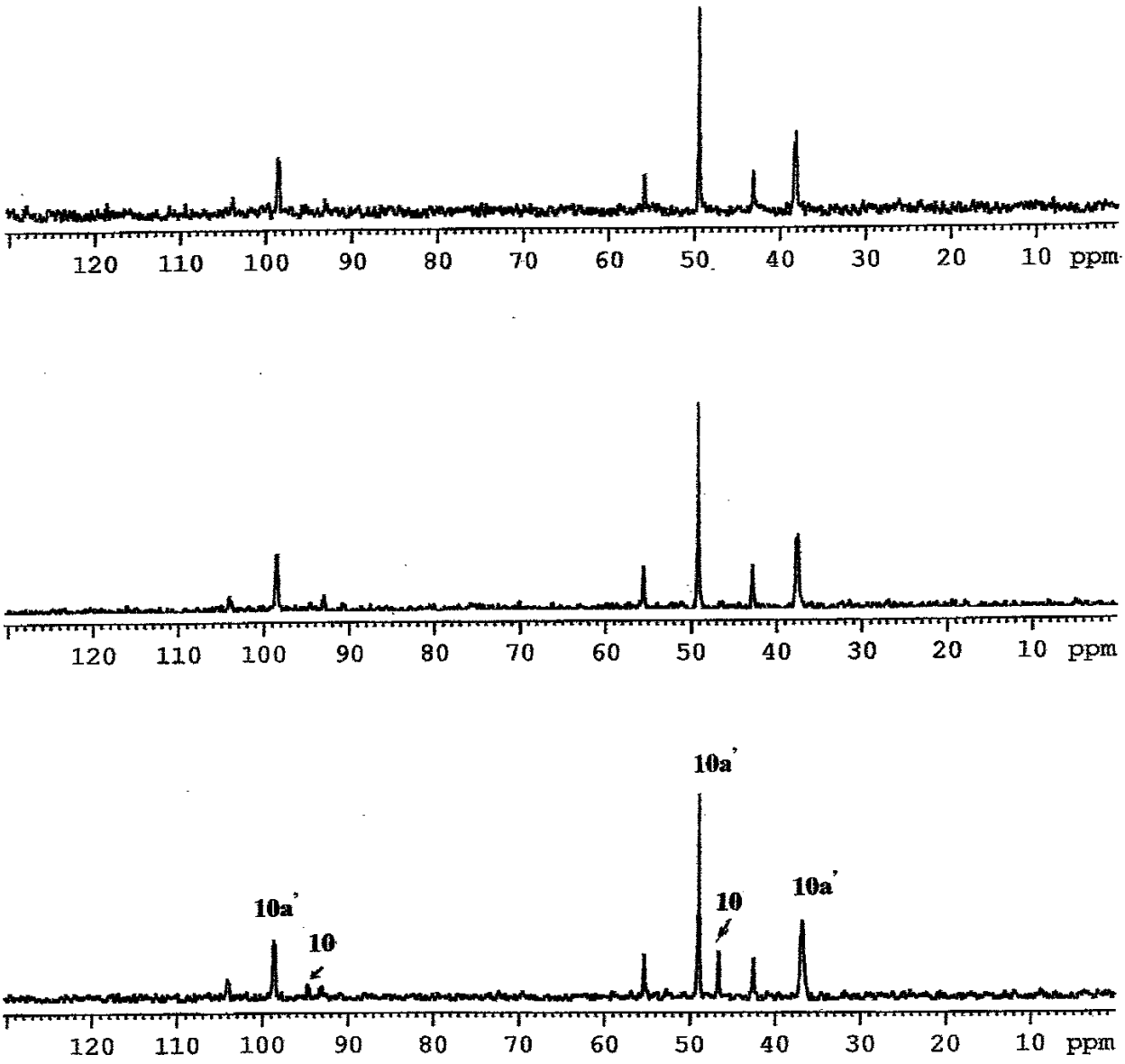
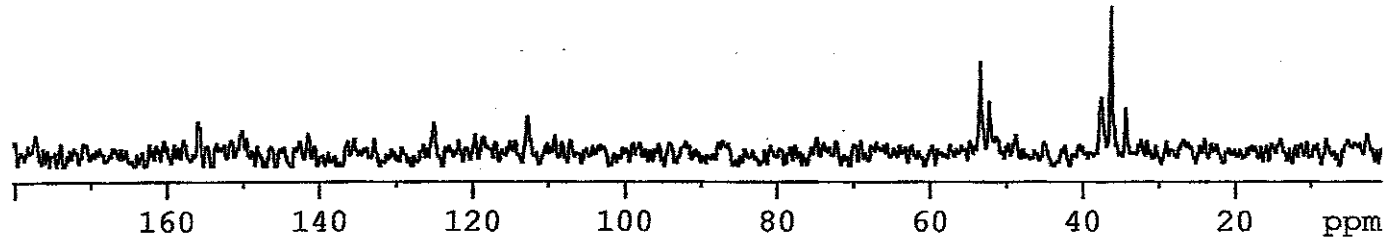
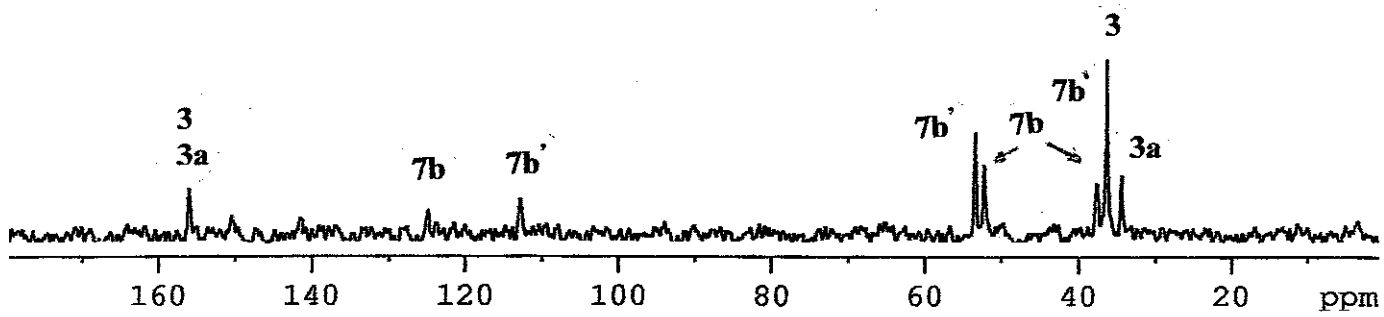


Figure S8





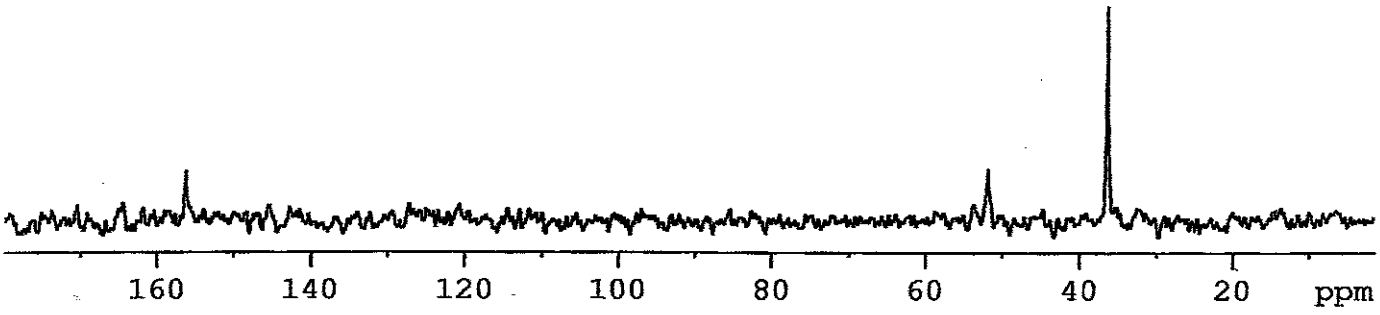


Figure S9

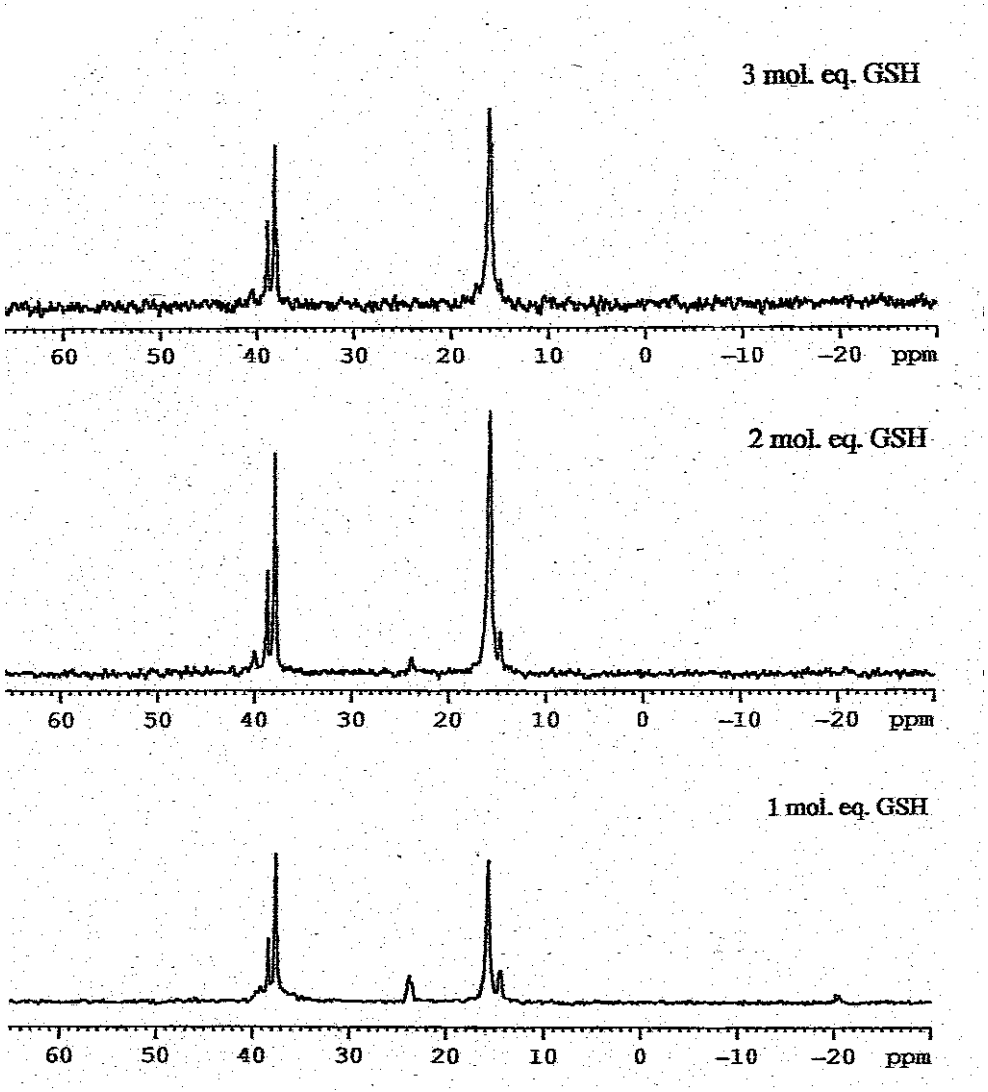


Figure S10