

## Supporting Information

### **( $\eta^6$ -Benzene)chromium Tricarbonyl and Cymantrene Assemblies Supported on an Organostannoxane Platform**

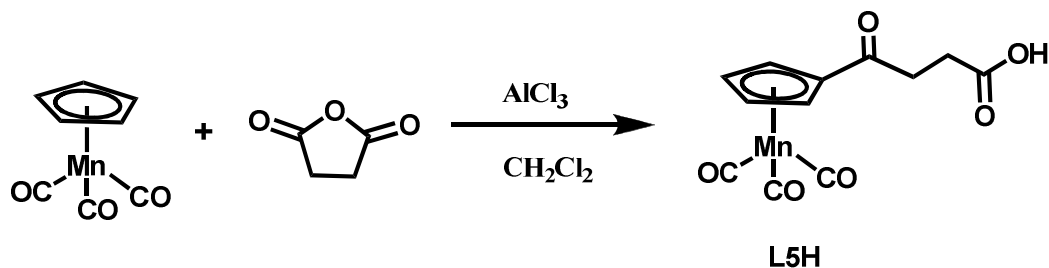
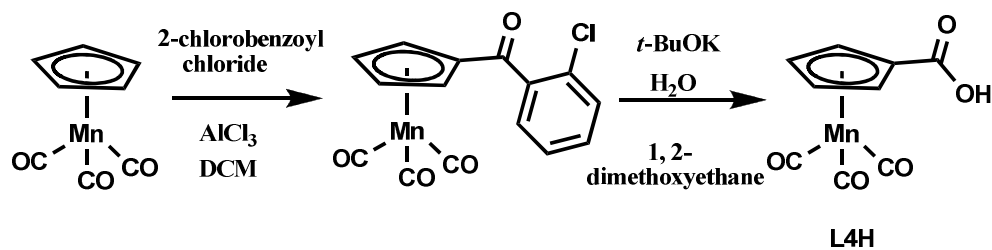
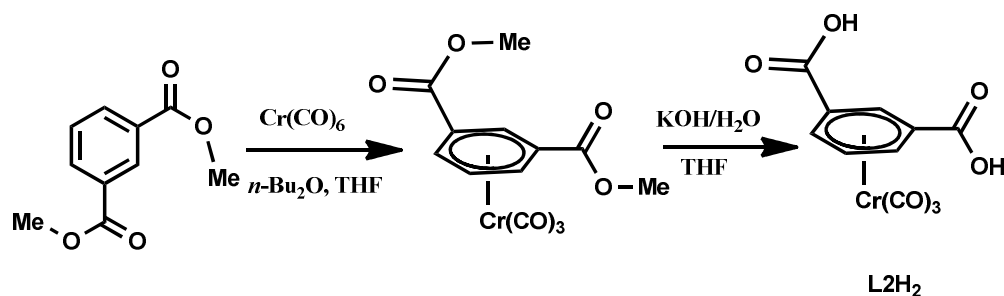
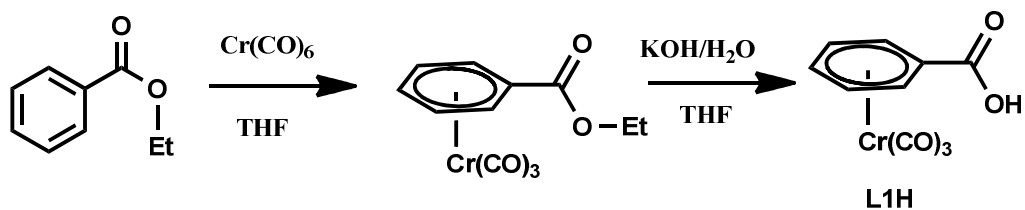
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## Synthesis of ligands:



**$[(\eta^6\text{-C}_6\text{H}_5\text{CO}_2\text{H})\text{Cr}(\text{CO})_3]$  (L1H):** A solution containing ethyl benzoate (3.0 g, 19.9 mmol) and  $\text{Cr}(\text{CO})_6$  (5.7 g, 25.9 mmol) in deoxygenated di-*n*-butyl ether (30 mL) and THF (3 mL) was refluxed for 72h under a  $\text{N}_2$  atmosphere under dark conditions. The sublimated  $\text{Cr}(\text{CO})_6$  was allowed to go back into the solution by mechanical stirring during the reaction. Upon cooling, the mixture was filtered through silica gel to remove unreacted and oxidized chromium products.

After removal of the solvents, the resulting orange solid was purified by column chromatography using a hexane: ethyl acetate (95:5) mixture under dark and the yield (2.6 g, 45%) obtained was used for the next step without further characterization.

L1H was prepared by saponification of the ester complex. Thus, to a deoxygenated solution of KOH (0.50 g, 8.9 mmol) in THF (40 mL) and deionized water (15 mL) was added the ester 1.0 g (3.5 mmol). The solution was stirred overnight under N<sub>2</sub>. To the resulting yellow solution was added 15 mL of deionized water. The aqueous phase was separated and washed with diethyl ether (40 mL). The aqueous component containing the organometallic salt K[Cr{ $\eta^6$ -C<sub>6</sub>H<sub>5</sub>(CO<sub>2</sub>)(CO)<sub>3</sub>] was treated with dil. HCl (10%) until a pH of *ca.* 2 was obtained. The product, L1H, was extracted into diethyl ether (2 × 50 mL) and dried using anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated to get a red-orange colored product. Yield: (0.78 g, 86%). <sup>1</sup>H NMR [500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, ppm]: 5.22 (t, 2H), 5.48 (t, 1H), 6.05 (d, 2H).

[{ $\eta^6$ -C<sub>6</sub>H<sub>4</sub>(COOH)<sub>2-1,3</sub>}Cr(CO)<sub>3</sub>](L2H<sub>2</sub>): L2H<sub>2</sub> was prepared from dimethylisophthalate [C<sub>6</sub>H<sub>4</sub>(CO<sub>2</sub>Me)<sub>2-1,3</sub>] and Cr(CO)<sub>6</sub> using a procedure identical to that for the preparation of L1H. Overall yield: 40%. <sup>1</sup>H NMR [500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, ppm]: 5.50 (t, 1H), 6.40 (d, 2H), 6.82 (s, 1H).

[{ $\eta^6$ -C<sub>6</sub>H<sub>4</sub>(COOH)<sub>2-1,4</sub>}Cr(CO)<sub>3</sub>](L3H<sub>2</sub>): L3H<sub>2</sub> was prepared from dimethylterephthalate [C<sub>6</sub>H<sub>4</sub>(COOH)<sub>2-1,4</sub>] and Cr(CO)<sub>6</sub> using a procedure identical to that for the preparation of the acid L1H. Overall yield: 38%. <sup>1</sup>H NMR [500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, ppm]: 6.20 (s, 4H).

[{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>C(O)C<sub>6</sub>H<sub>4</sub>Cl}Mn(CO)<sub>3</sub>]: Cymantrene (1.0 g, 4.50 mmol) and anhydrous dichloromethane (40 mL) were placed in a 100 mL roundbottom flask. To the magnetically stirred and cooled (0–5 °C) solution was added 2-chlorobenzoyl chloride (0.80 g, 4.57 mmol).

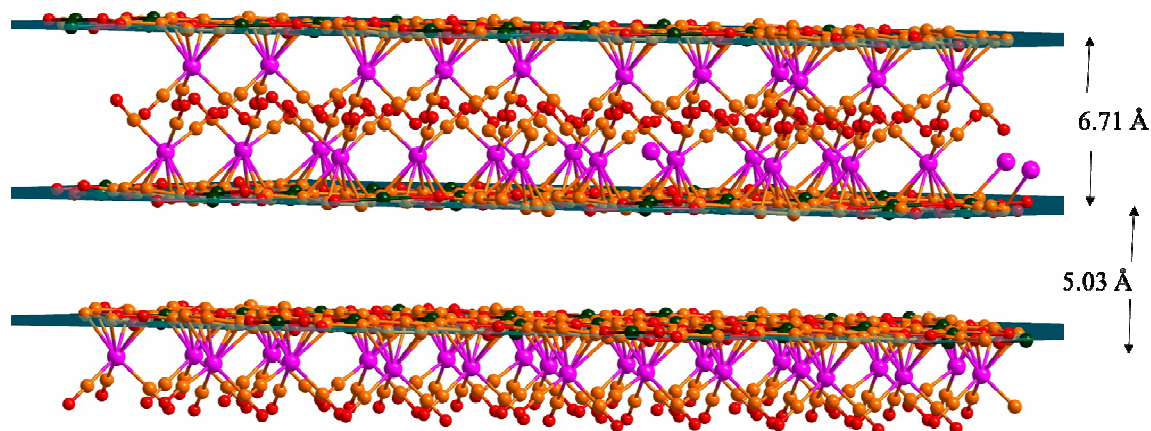
Then, anhydrous aluminium chloride (0.90 g, 6.75 mmol) was added in small portions at 0–5 °C. The stirring was continued overnight at room temperature. Throughout the ensuing reaction the system is maintained under positive pressure of dry nitrogen. The reaction mixture was then poured into a mixture of ice-water (40 mL). The layers were separated and the aqueous phase extracted with dichloromethane (2×40 mL). The combined organic extracts were washed with water and finally with 30 mL 10% aqueous sodium hydroxide. The organic solution was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated. The product was purified by column chromatography on silica using a mixture of hexane-ethyl acetate 5 : 3 (v/v) as the eluent.

Yield: 1.3 g (80%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) (δ, ppm): 4.88 (s, 2H), 5.36 (s, 2H), 7.36-7.43 (m, 4H).

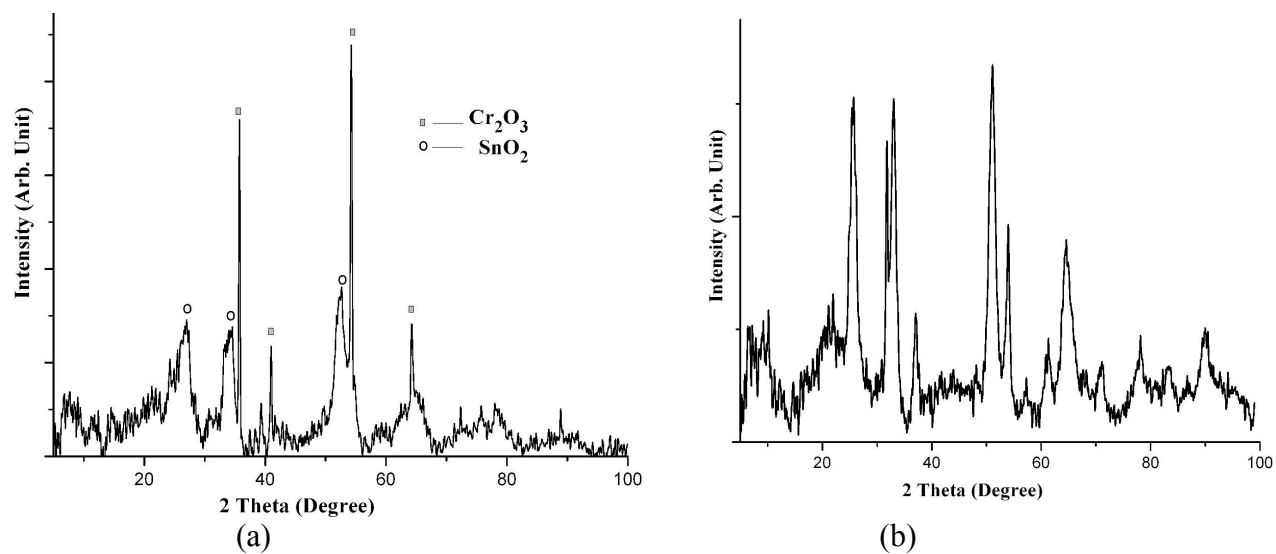
**[( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>COOH)Mn(CO)<sub>3</sub>] (L4H):** (2-chlorobenzoyl)cymantrene (1.3 g, 3.61 mmol) potassium *tert*-butoxide (0.60 g, 5.41 mmol) and dry 1,2-dimethoxyethane (30 mL) were taken in a 100 mL roundbottom flask under dry nitrogen atmosphere. Water (65 μL, 3.61 mmol) was added. The red solution is stirred and refluxed under nitrogen for overnight. The reaction mixture is cooled and poured into 30 mL of water. The resulting solution was washed with (2×30 mL) DCM. The aqueous phase was acidified and the cymantrene carboxylic acid extracted with ether (2×30 mL). The combined ether solutions dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was then removed in vacuum. Yield: 0.70g (72%); <sup>1</sup>H NMR (500 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, 25 °C) (δ, ppm): 5.10 (s, 2H), 5.57 (s, 2H).

**[( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>C(O)CH<sub>2</sub>CH<sub>2</sub>COOH)Mn(CO)<sub>3</sub>] (L5H):** In a 100 mL roundbottom flask was placed cymantrene (1.0 g, 4.50 mmol) and anhydrous dichloromethane (40 mL). To the magnetically stirred and cooled (0–5 °C) solution was added succinic anhydride (0.45 g, 4.50 mmol). Then,

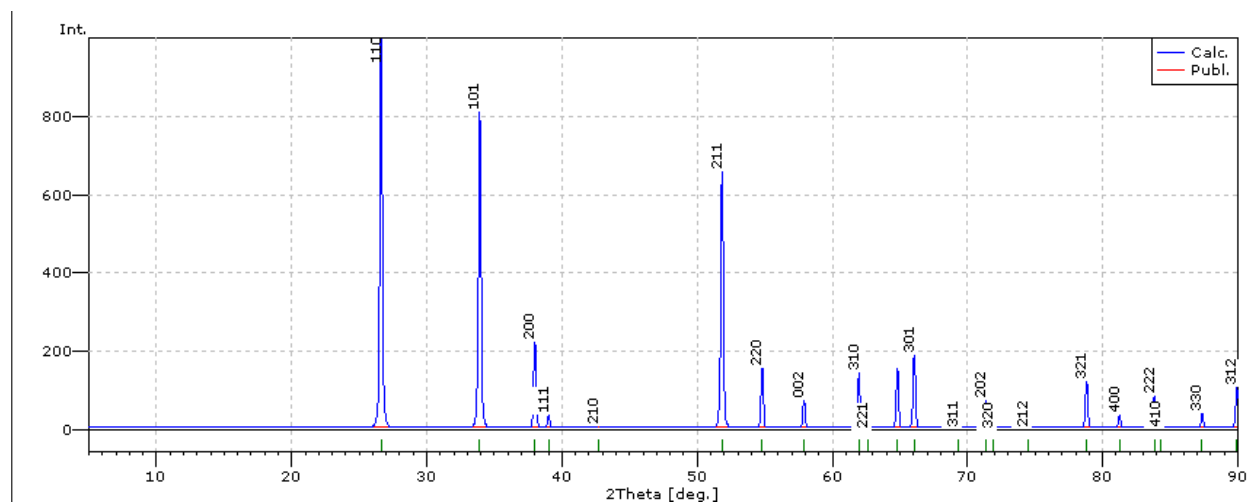
anhydrous aluminium chloride (0.90 g, 6.75 mmol) was added in small portions at 0–5 °C. The stirring was continued overnight at room temperature. The reaction mixture was then poured into a mixture of ice-water (40 mL) and concentrated hydrochloric acid (5 mL). The layers were separated and the aqueous phase extracted with dichloromethane (2×40 mL). The combined organic extracts were washed with water and finally with 30 mL aqueous sodium carbonate solution (20%). The aqueous phase was acidified and the cymantrene keto carboxylic acid extracted with ether (2×30 mL). The combined ether solutions dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was then removed in vacuum and the crude product recrystallized from a tetrahydrofuran/pentane mixture. Yield: 1.1 g (80%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) (δ, ppm): 2.50 (s, 2H), 2.83 (s, 2H), 4.84 (s, 2H), 5.46 (s, 2H).



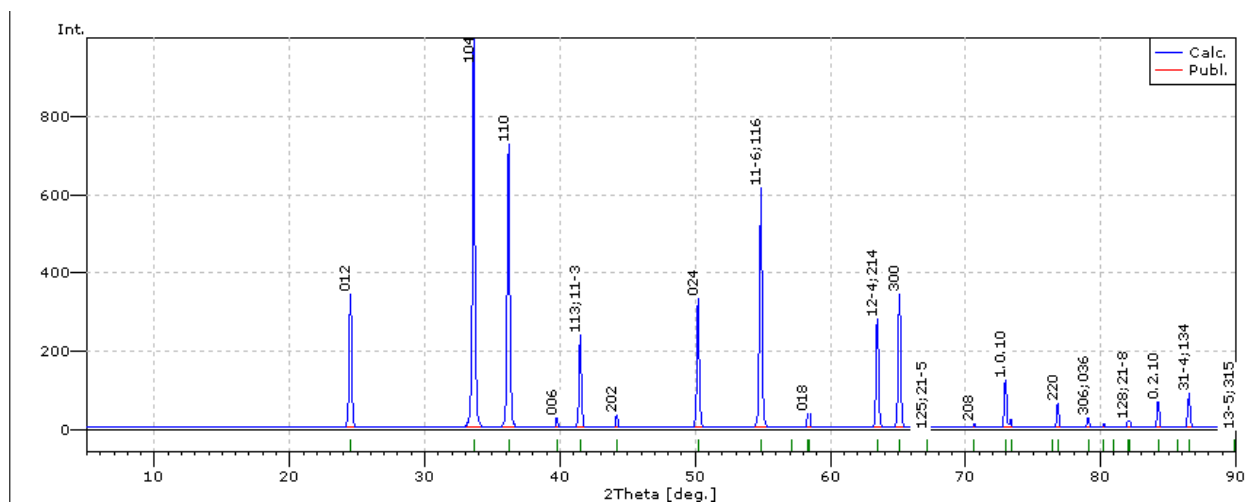
**Figure S1:** Packing of **5**.



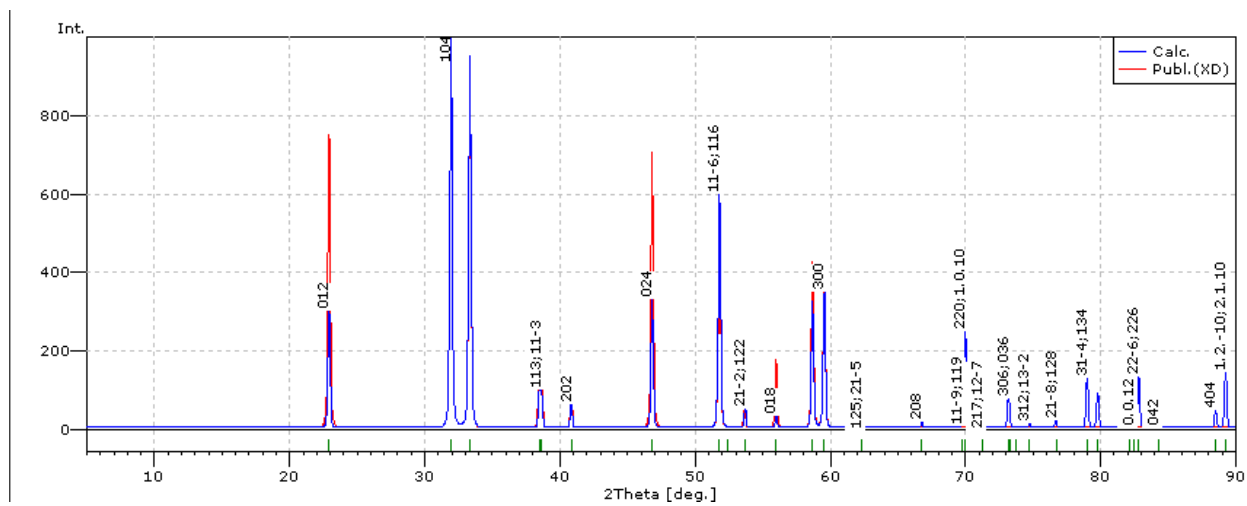
**Figure S2:** (a) XRD patterns of  $\text{Cr}_2\text{O}_3$  and  $\text{SnO}_2$  mixture (b) XRD patterns of  $\text{MnSnO}_3$  binary oxide.



**Figure S3:** XRD patterns of  $\text{SnO}_2$  (Reference : PCD entry no 1824248)



**Figure S4:** XRD patterns of  $\text{Cr}_2\text{O}_3$  (Reference : PCD entry no 1624522)



**Figure S5:** XRD patterns of  $\text{MnSnO}_3$  (Reference : PCD entry no 307504)

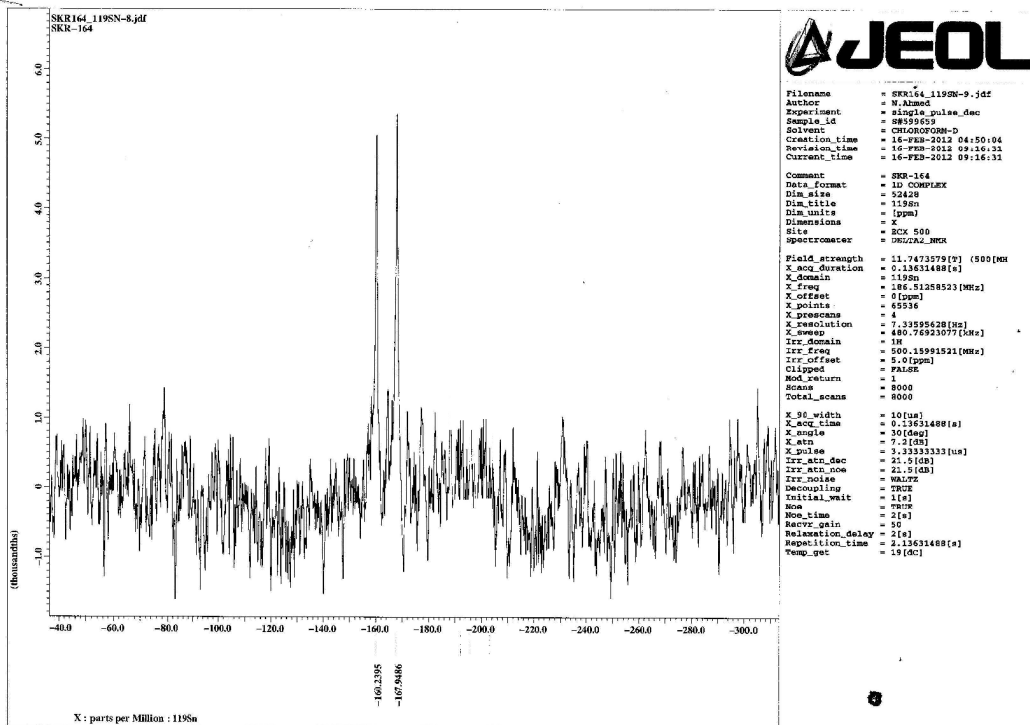


Figure S6:  $^{119}\text{Sn}$  NMR of 1.

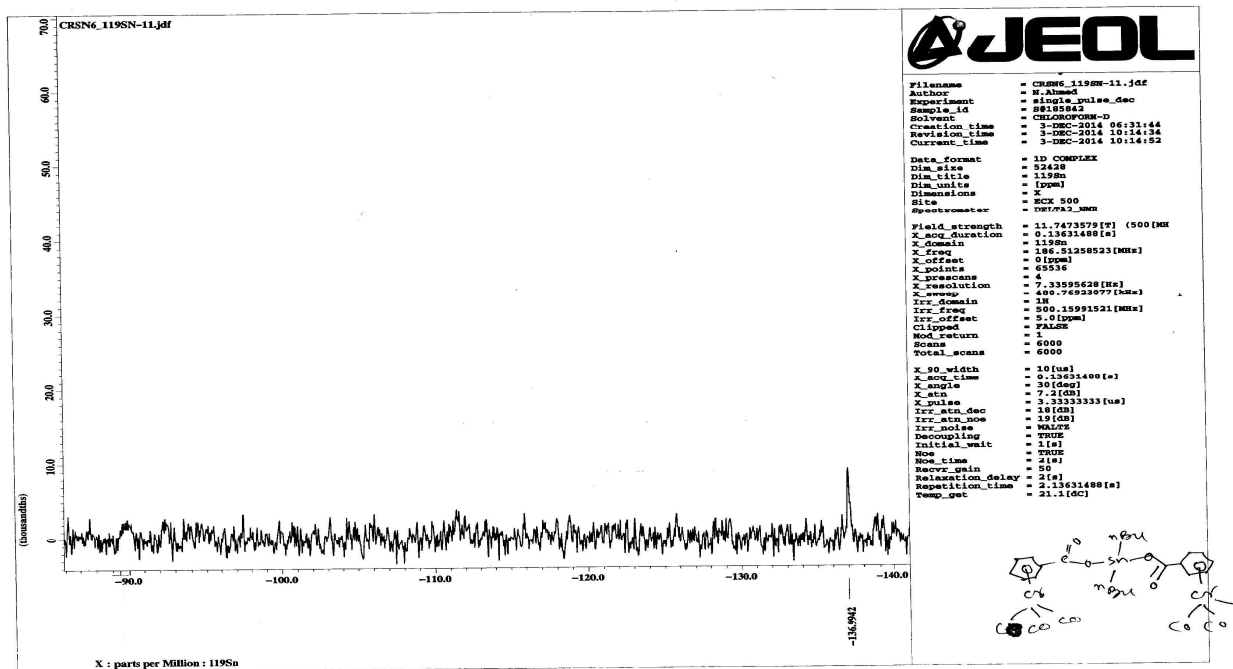


Figure S7:  $^{119}\text{Sn}$  NMR of 2.

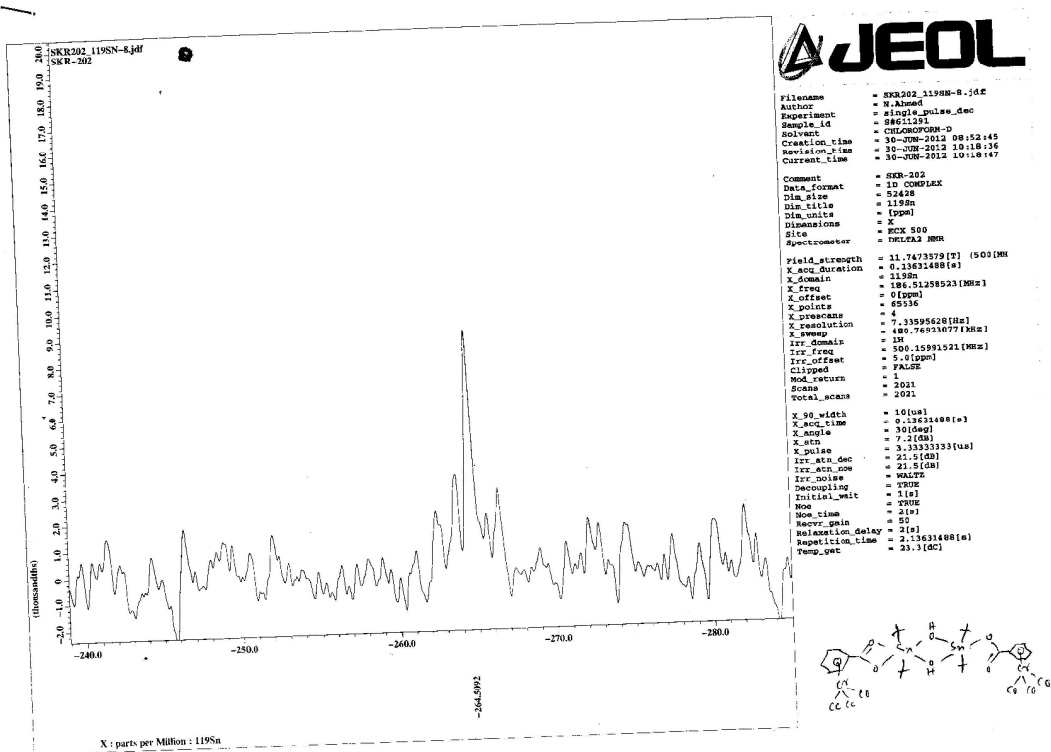


Figure S8:  $^{119}\text{Sn}$  NMR of 3.

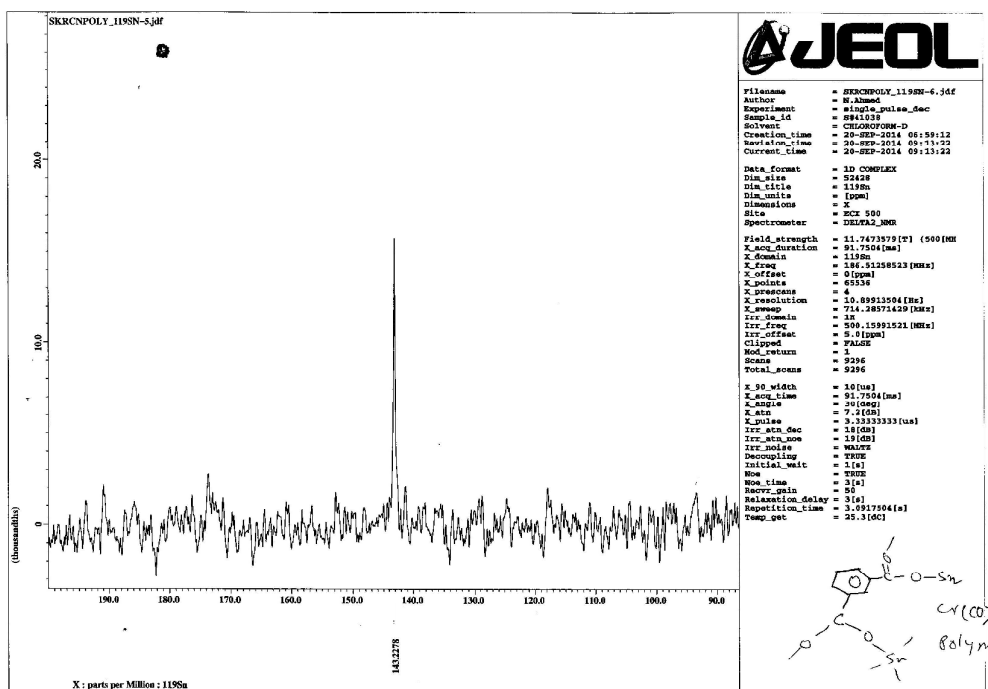


Figure S9:  $^{119}\text{Sn}$  NMR of 4.

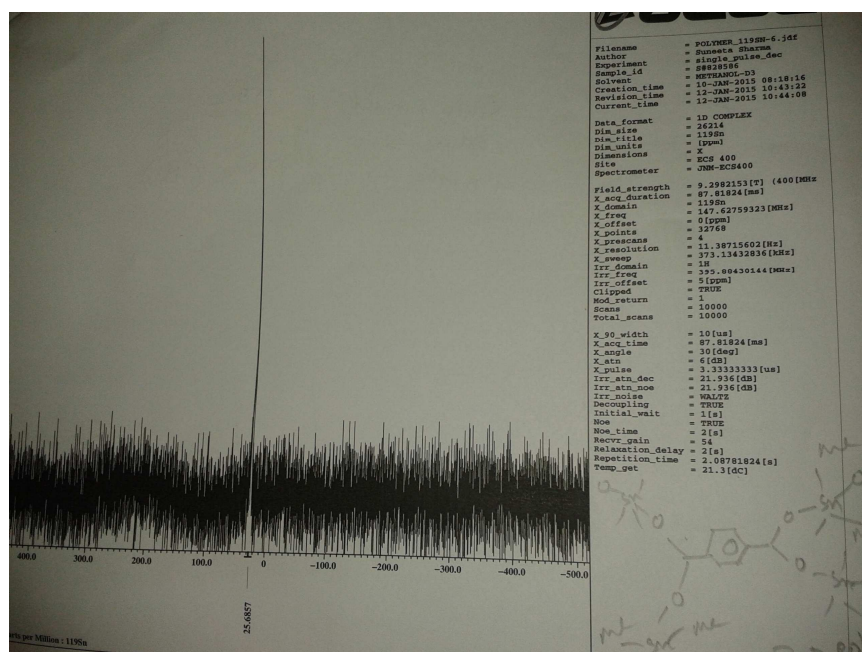


Figure S10:  $^{119}\text{Sn}$  NMR of 5.

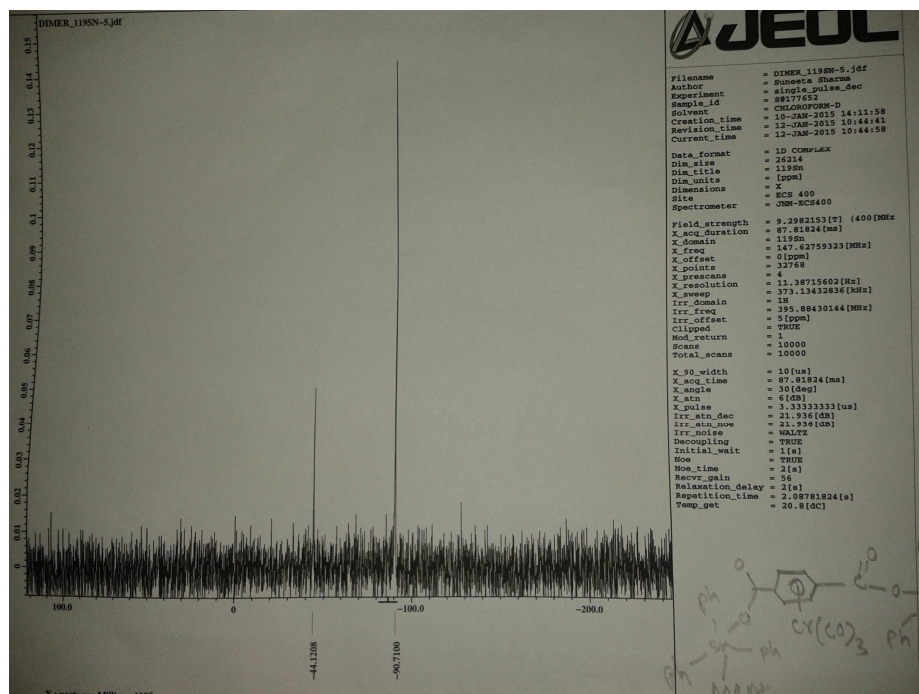


Figure S11:  $^{119}\text{Sn}$  NMR of 7.

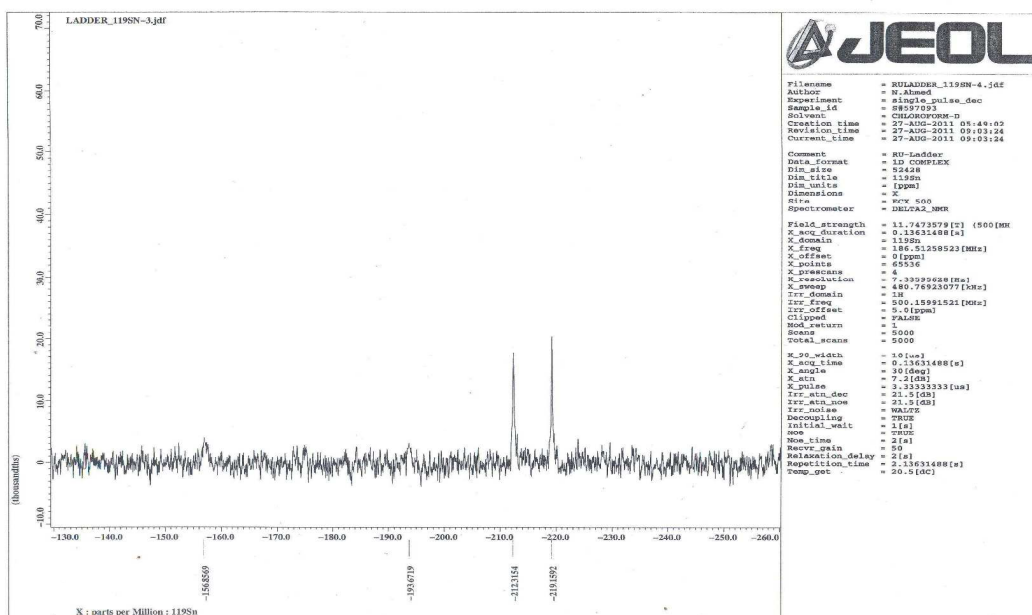


Figure S12:  $^{119}\text{Sn}$  NMR of 8.

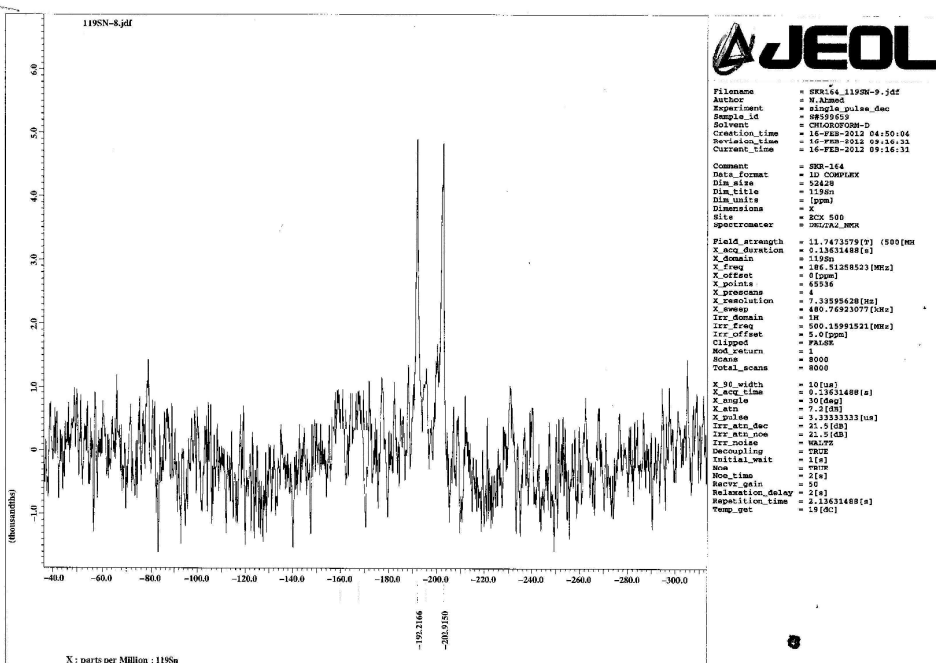
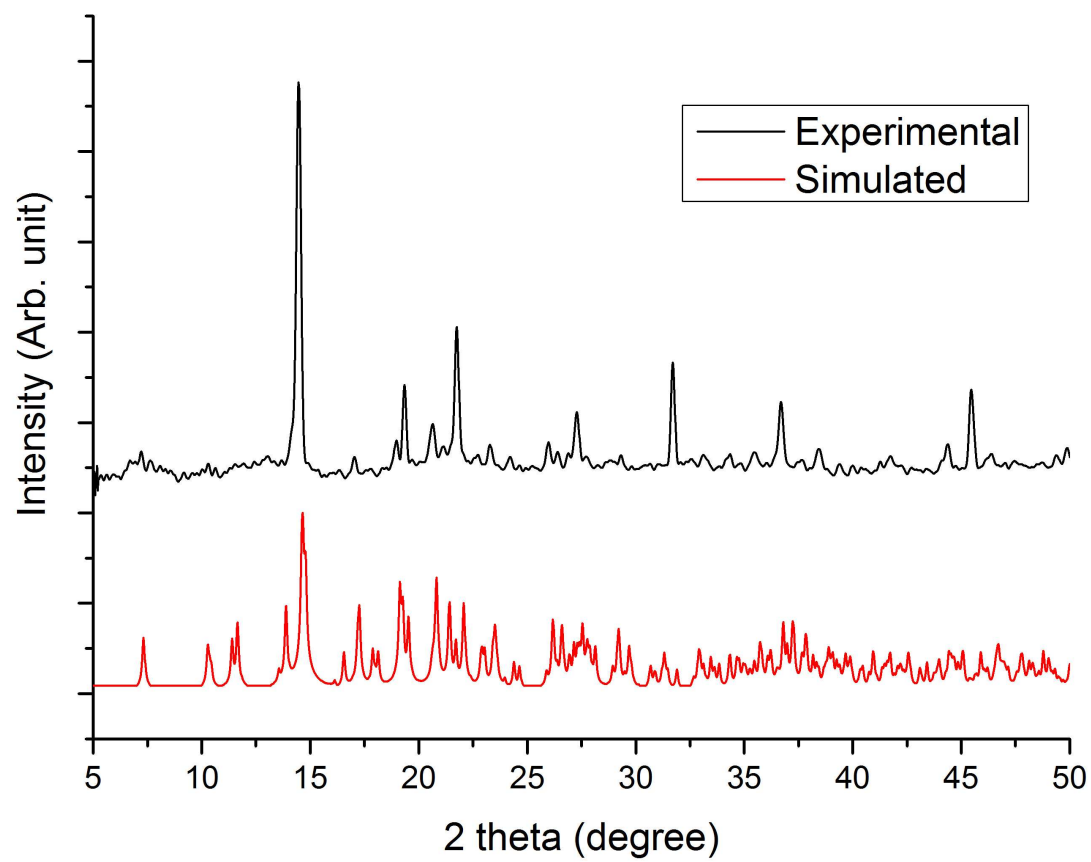
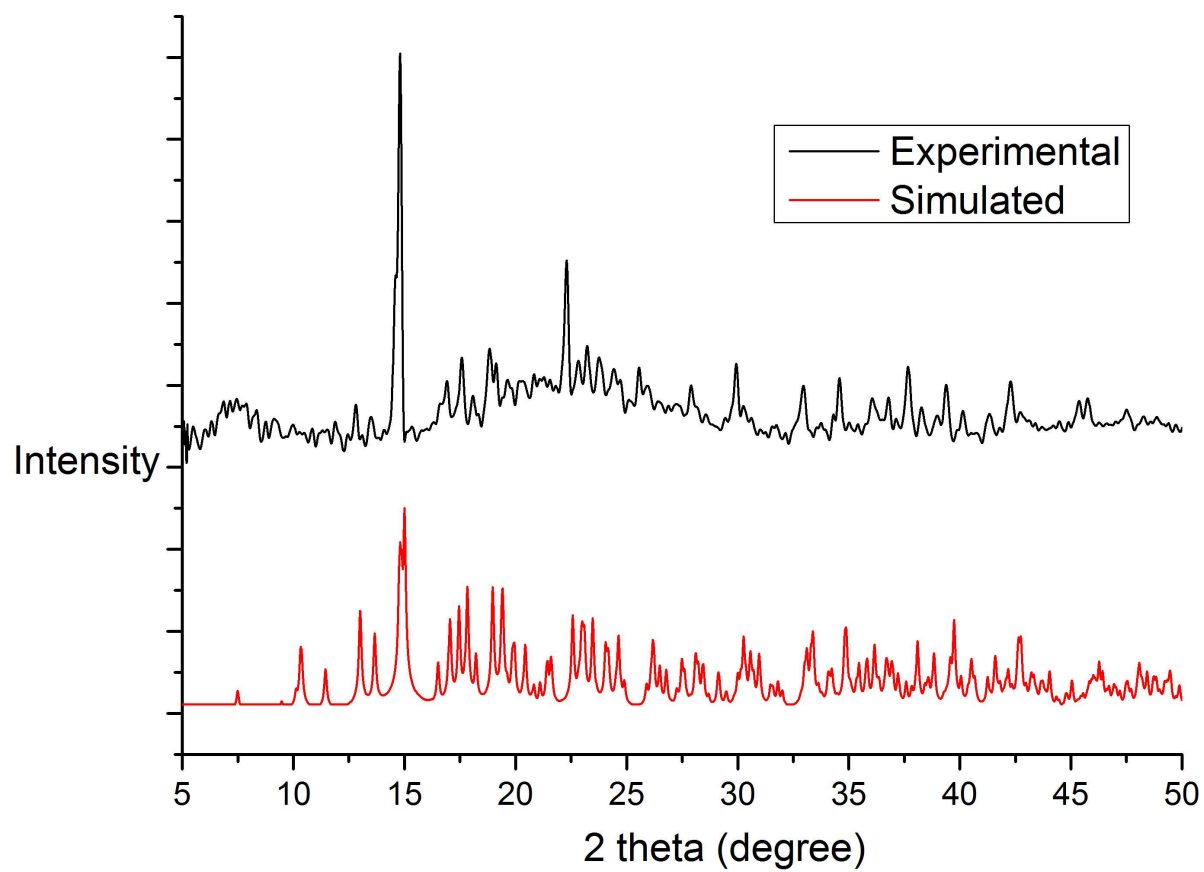


Figure S13:  $^{119}\text{Sn}$  NMR of 9.



**Figure S13:** PXRD pattern of polymer 4.



**Figure S13:** PXRD pattern of polymer **5**.