

# *Supporting Information*

## **Tuning a Cr-Catalyzed Ethylene Oligomerization Product Profile via a Rational Design of the N-aryl PNP Ligands**

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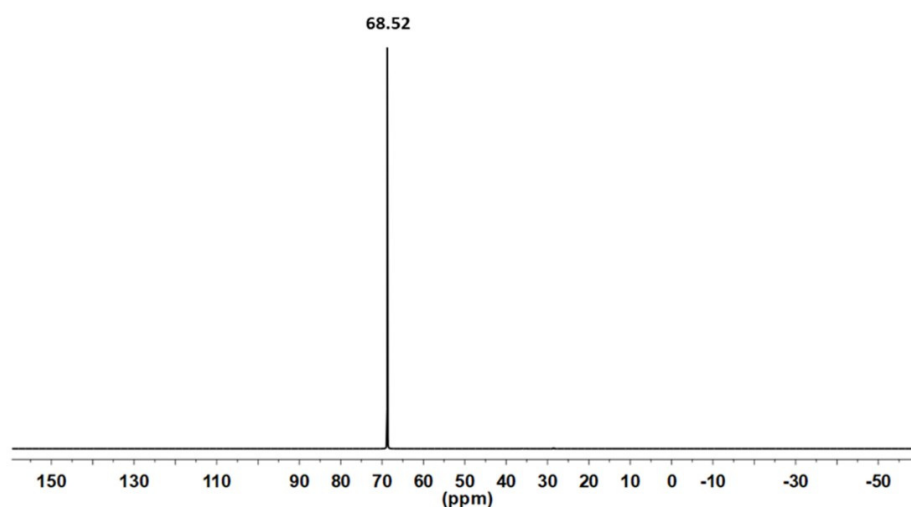
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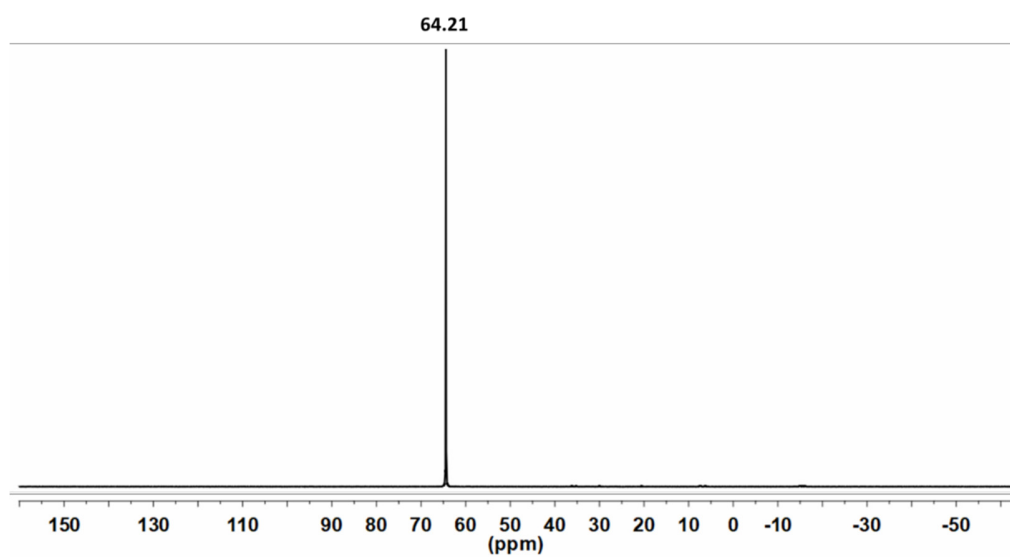
## Section S1 General Comments

All manipulations were performed under an inert atmosphere of dry argon using standard Schlenk techniques. Solvents,  $\text{Ph}_2\text{PCl}$ ,  $\text{Et}_3\text{N}$ , amine precursors and other chemicals were purchased from Sigma Aldrich. MMAO-3A (7 wt% solution in heptane) was purchased from Nouryon.  $\text{Cr}(\text{acac})_3$  (97% purity) was purchased from Strem chemicals. The ethylene gas (99.995% purity) was procured from Abdulla Hashim Gas Co., Saudi Arabia. Solvents and amines were dried using the appropriate reagents (sodium metal, calcium hydride and molecular sieve) and distilled under an argon atmosphere prior to use. Nuclear magnetic resonance (NMR) spectra were obtained at RT with a Bruker 400 MHz instrument using  $\text{SiMe}_4$  for  $^1\text{H}$  and  $^{13}\text{C}$  and 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  as external standards. GC/FID analyses Agilent Technologies 7890A. Column: PoraBOND, 60 m  $\times$  320  $\mu\text{m}$   $\times$  0.5  $\mu\text{m}$ . The GC oven temperature program for the PoraBOND column set was 40  $^\circ\text{C}$  (1 min hold), increased to 80  $^\circ\text{C}$  at a heating rate of 20  $^\circ\text{C}/\text{min}$  (1 min hold), then to 160  $^\circ\text{C}$  at a rate of 20  $^\circ\text{C}/\text{min}$  (5 min hold), and finally to 250  $^\circ\text{C}$  at a rate of 30  $^\circ\text{C}/\text{min}$  (25 min hold), for a total runtime of 41 min.

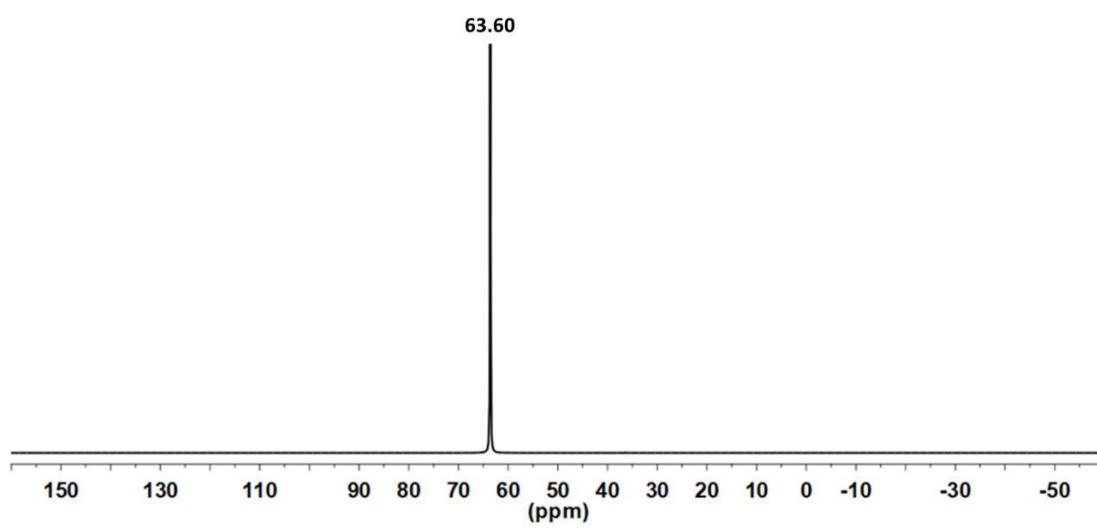
## Section S2 $^{31}\text{P}$ NMR spectra



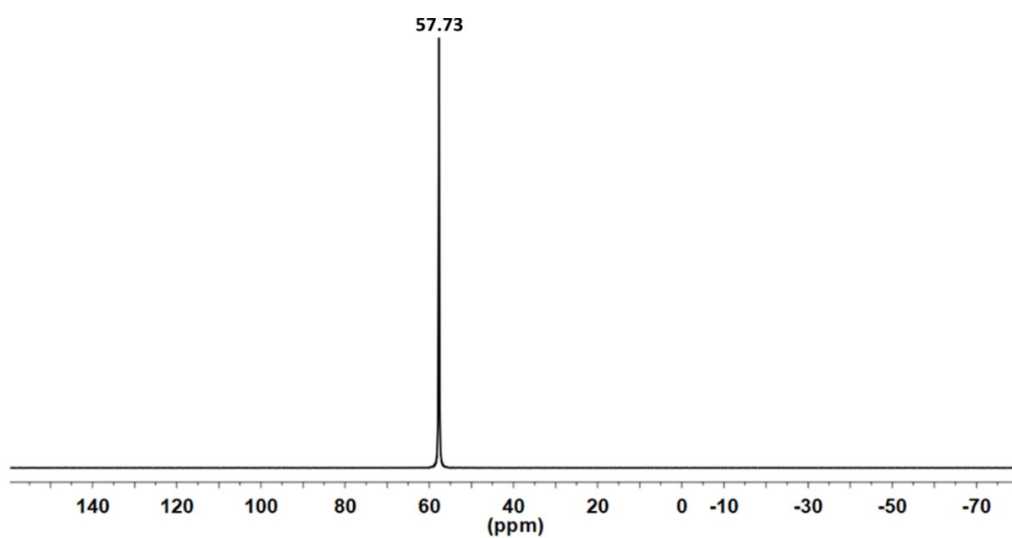
**Figure S1.**  $^{31}\text{P}$  NMR spectra of ligand 3.



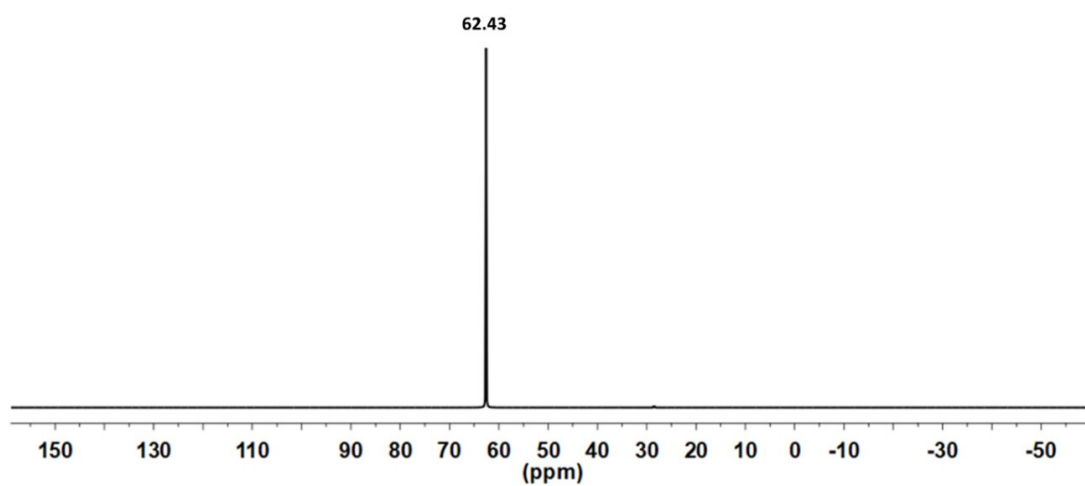
**Figure S2.**  $^{31}\text{P}$  NMR spectra of ligand 4.



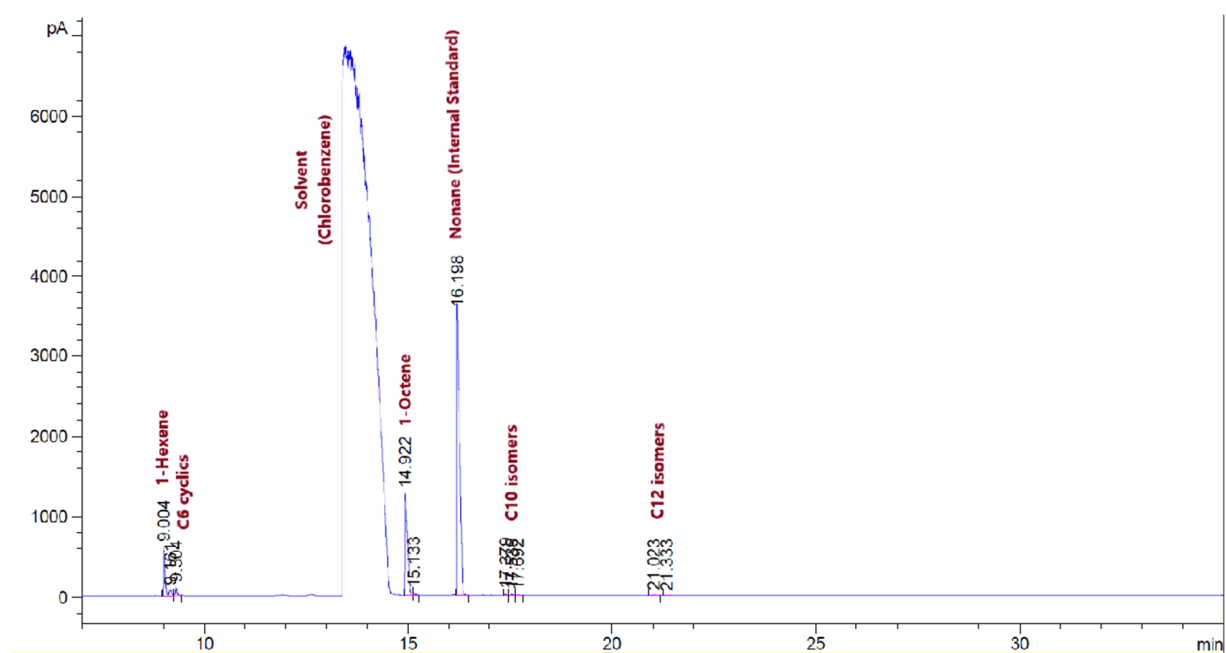
**Figure S3.**  $^{31}\text{P}$  NMR spectra of ligand 7.



**Figure S4.** The liquid state  $^{31}\text{P}$  NMR spectra of ligand 8.



**Figure S5.**  $^{31}\text{P}$  NMR spectra of ligand 9.



**Figure S6.** A GC traces of the aliquot collected after catalysis reaction using  $\text{Cr}(\text{acac})_3/1$  /MMAO- 3A system.