

Activation of metallocene hydride intermediates by methylaluminoxane in alkene dimerization and oligomerization

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Figure S1. ^1H NMR of system Cp_2HfCl_2 (**1b**) – HAlBu_2 (1:3) in C_7D_8 (298 K).

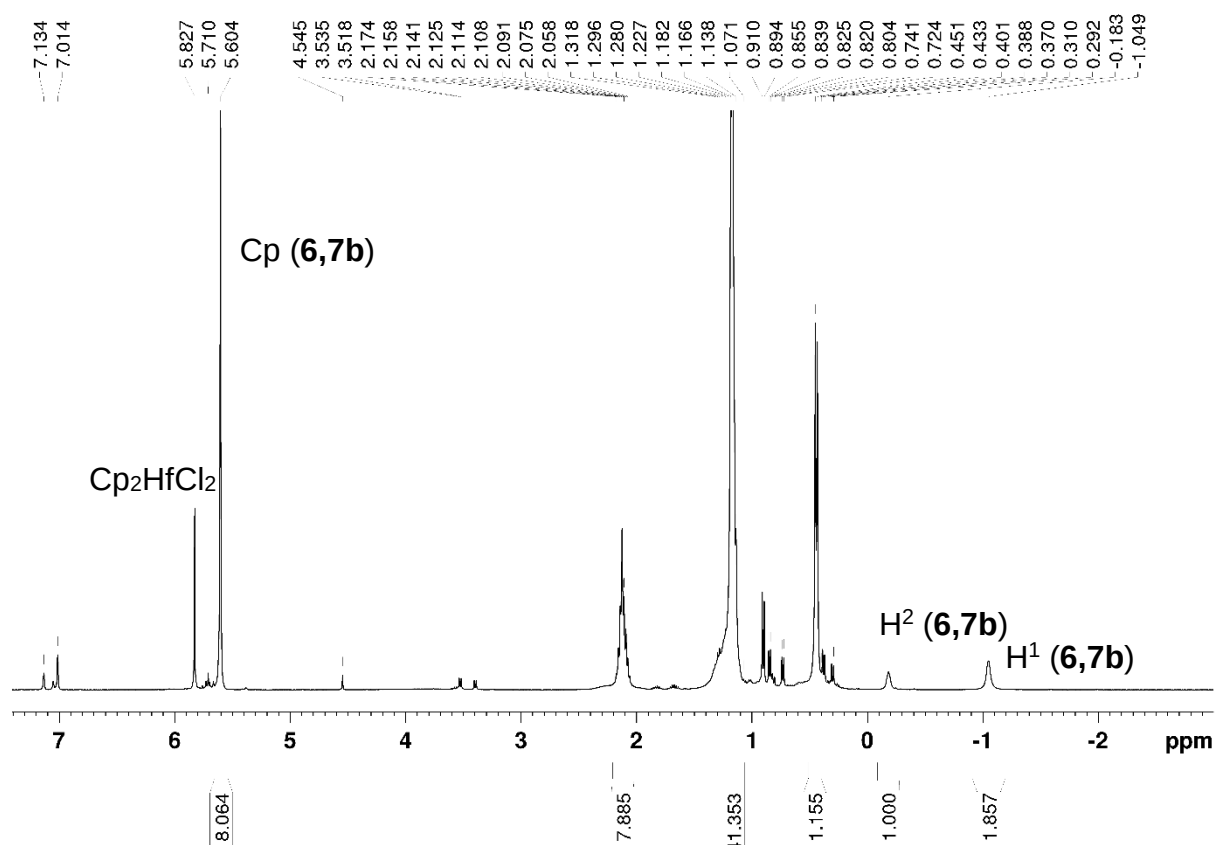


Figure S2. ^{13}C NMR of system Cp_2HfCl_2 (**1b**) – HAlBu_2 (1:3) in C_7D_8 (298 K).

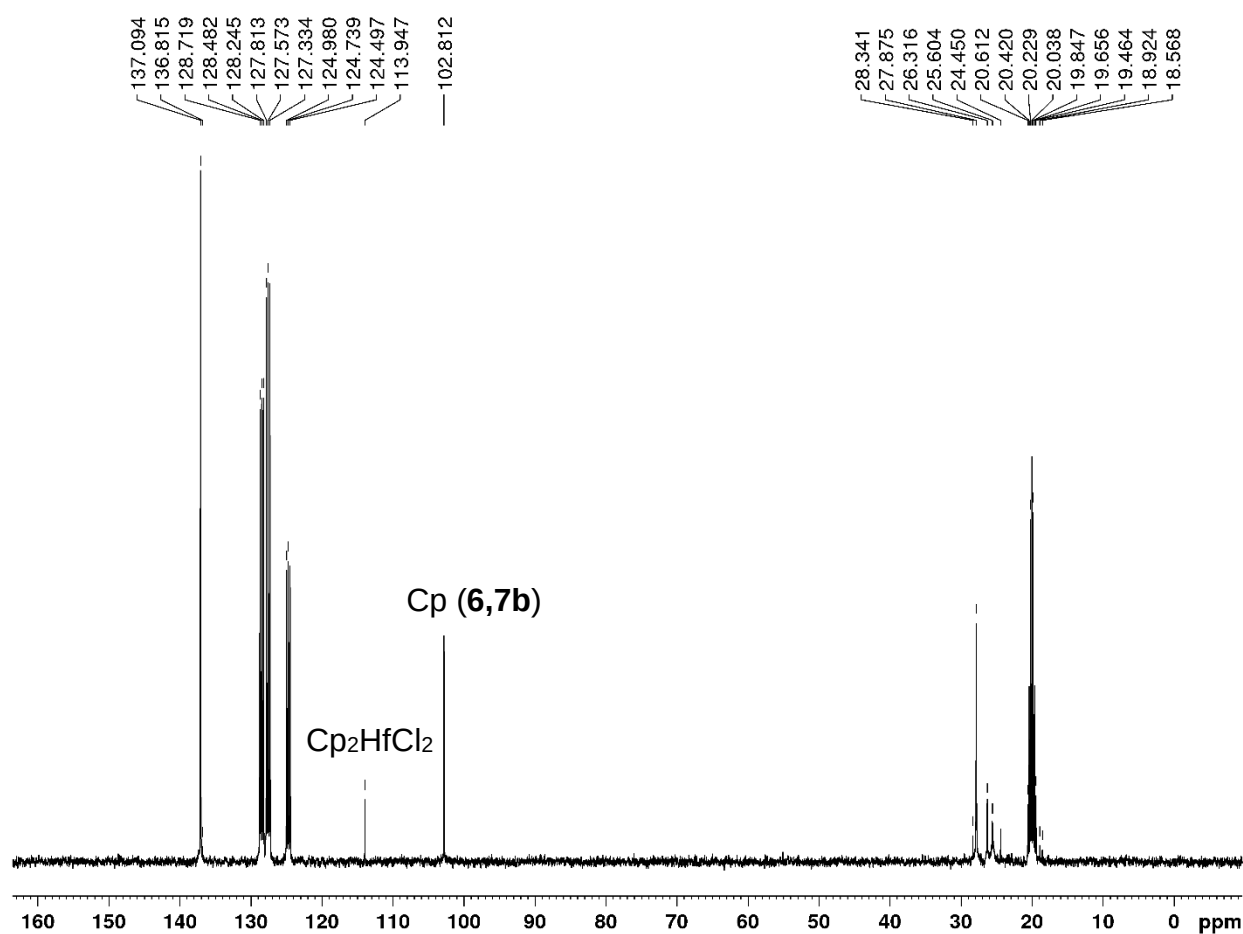


Figure S3. COSY HH of system Cp_2HfCl_2 (**1b**) – HAlBu_2 (1:3) in C_7D_8 (298 K).

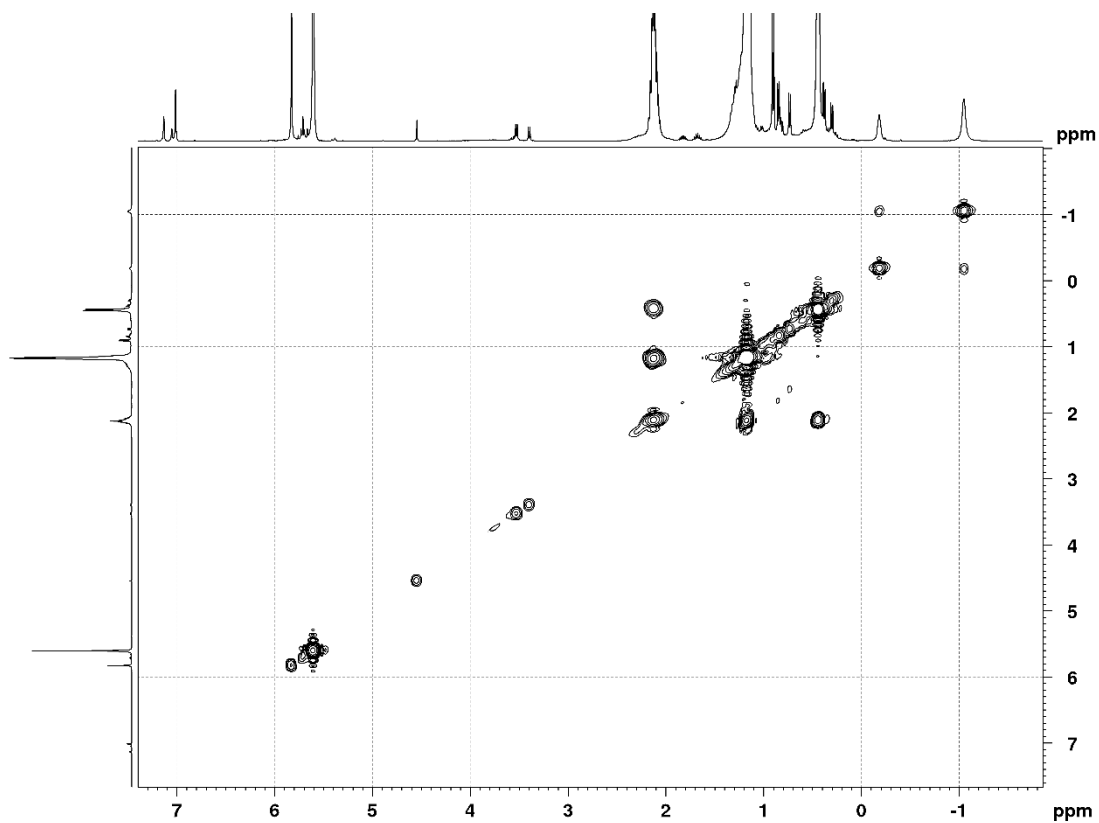


Figure S4. ^1H NMR of system Cp_2HfCl_2 (**1b**) – HAlBu_2 (1:14) in C_7D_8 (298 K).

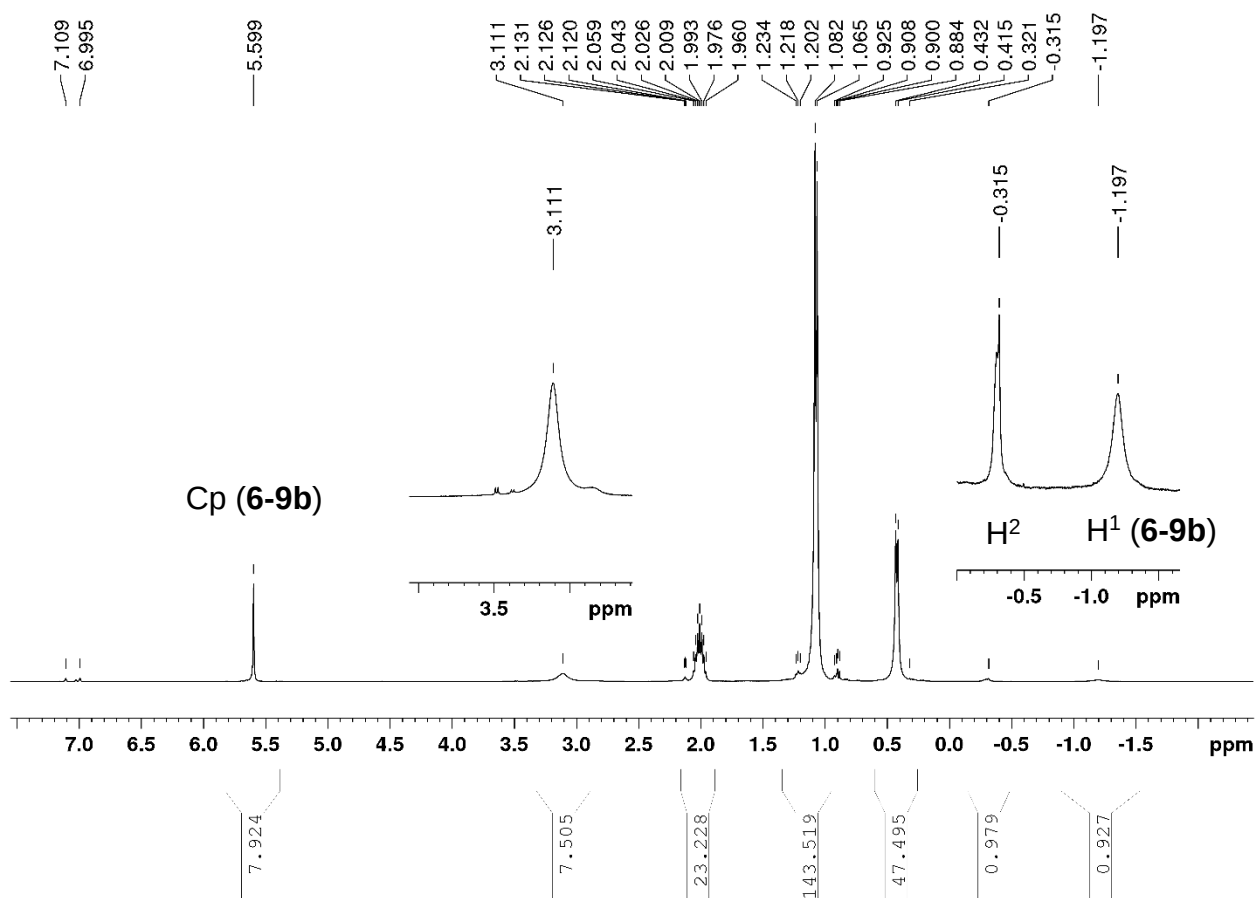


Figure S5. NOESY of system Cp_2HfCl_2 (**1b**) – HAlBu^i_2 (1:14) in C_7D_8 (298 K).

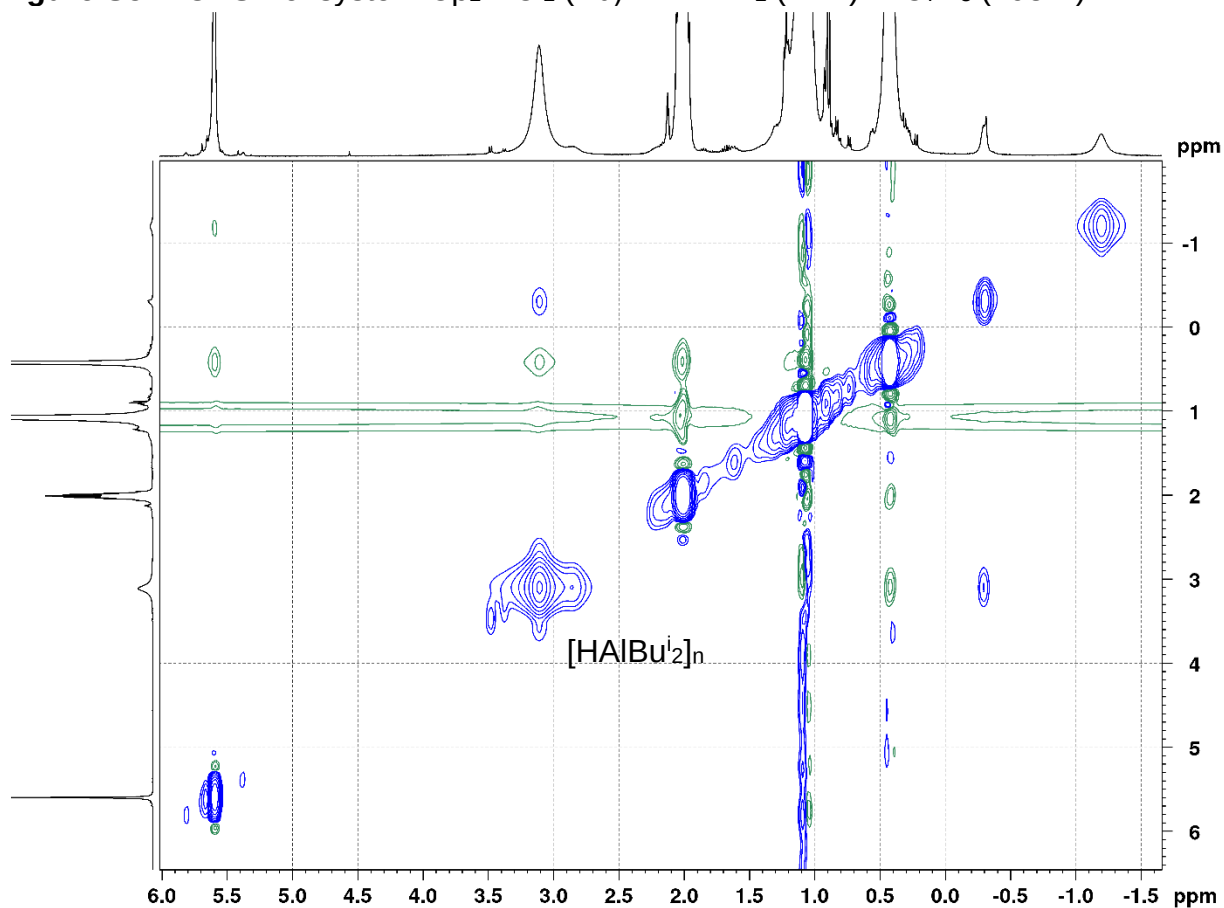


Figure S6. ^1H NMR of system Cp_2HfCl_2 (**1b**) – HAlBu^i_2 – MMAO-12 (1:14:9) in C_7D_8 (298 K).

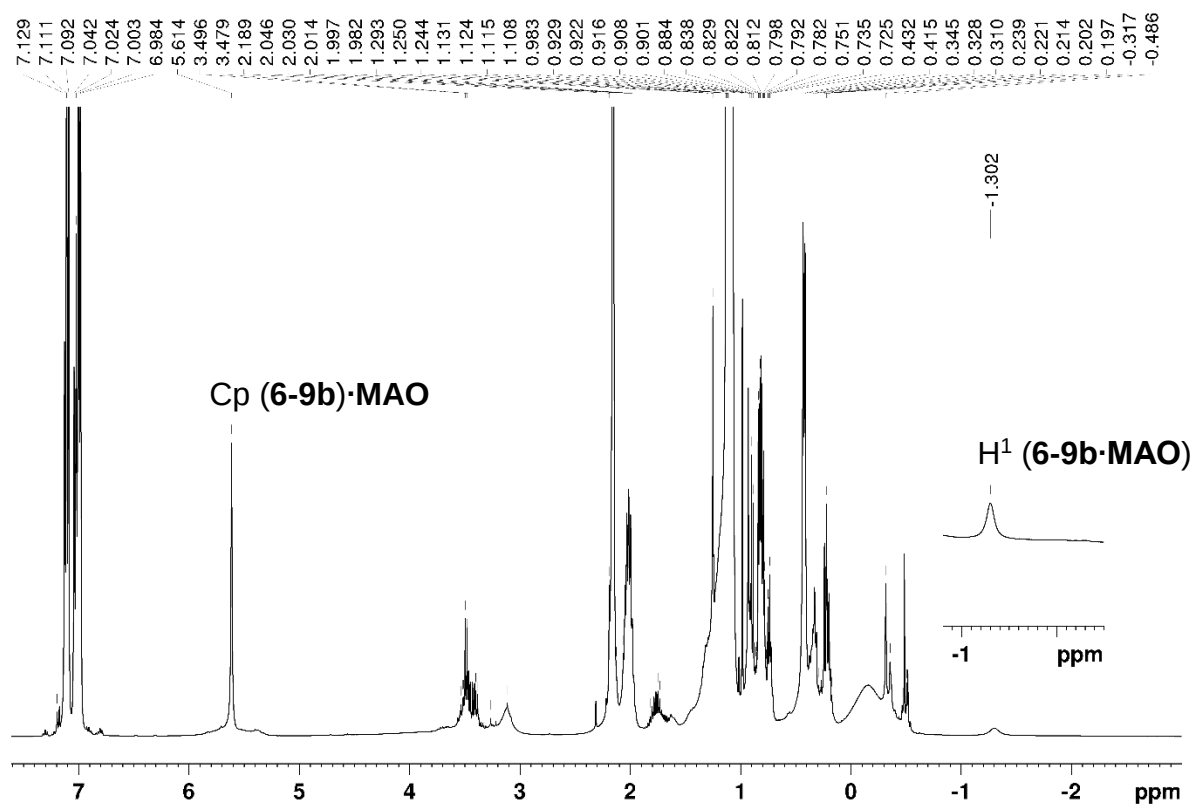


Figure S7. ^1H NMR of system Cp_2HfCl_2 (**1b**) – HAIBu^i_2 – MMAO-12 (1:4:13) in C_7D_8 (298 K).

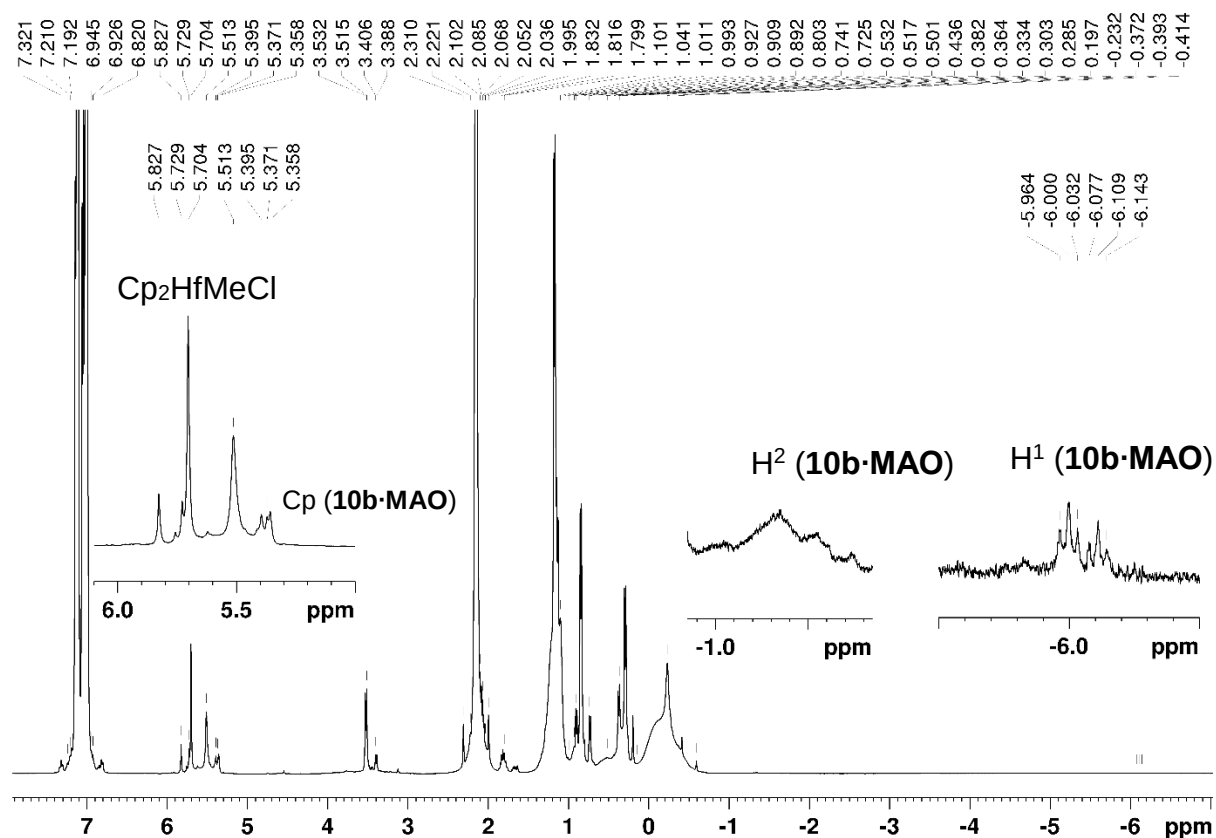


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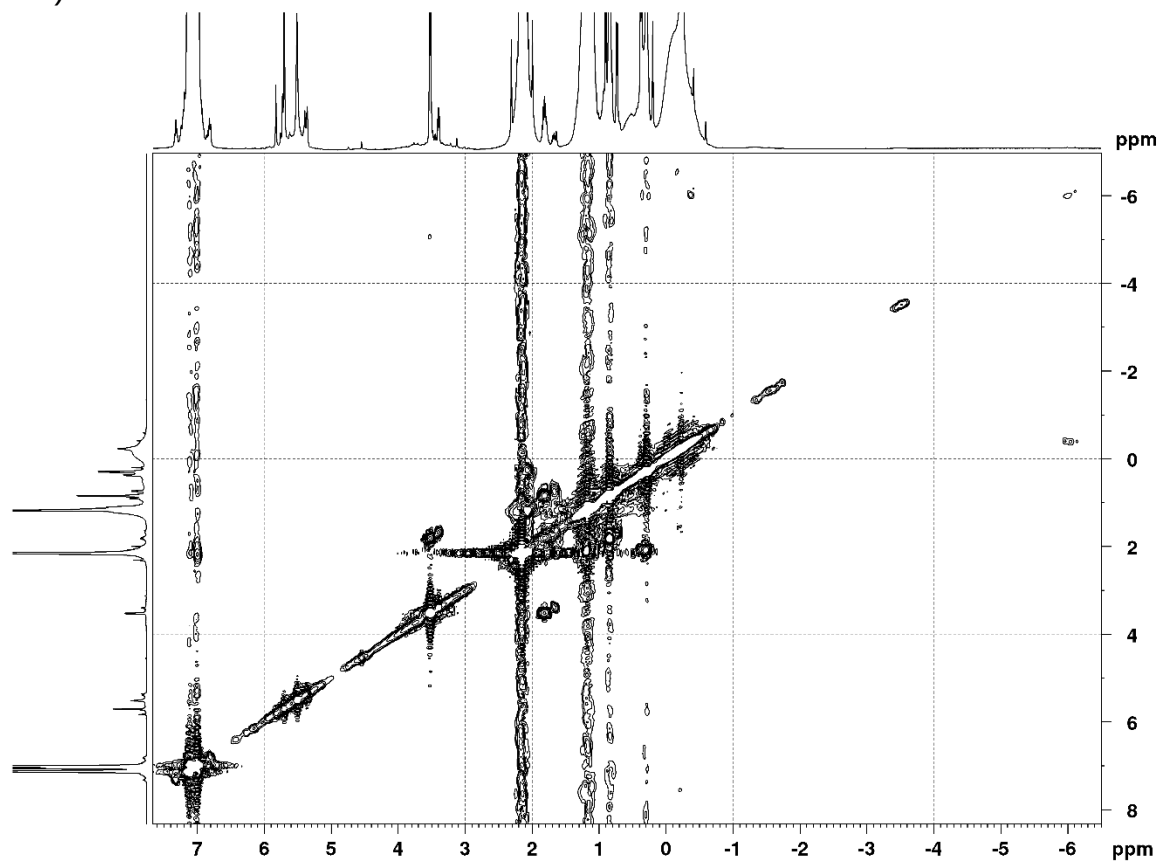


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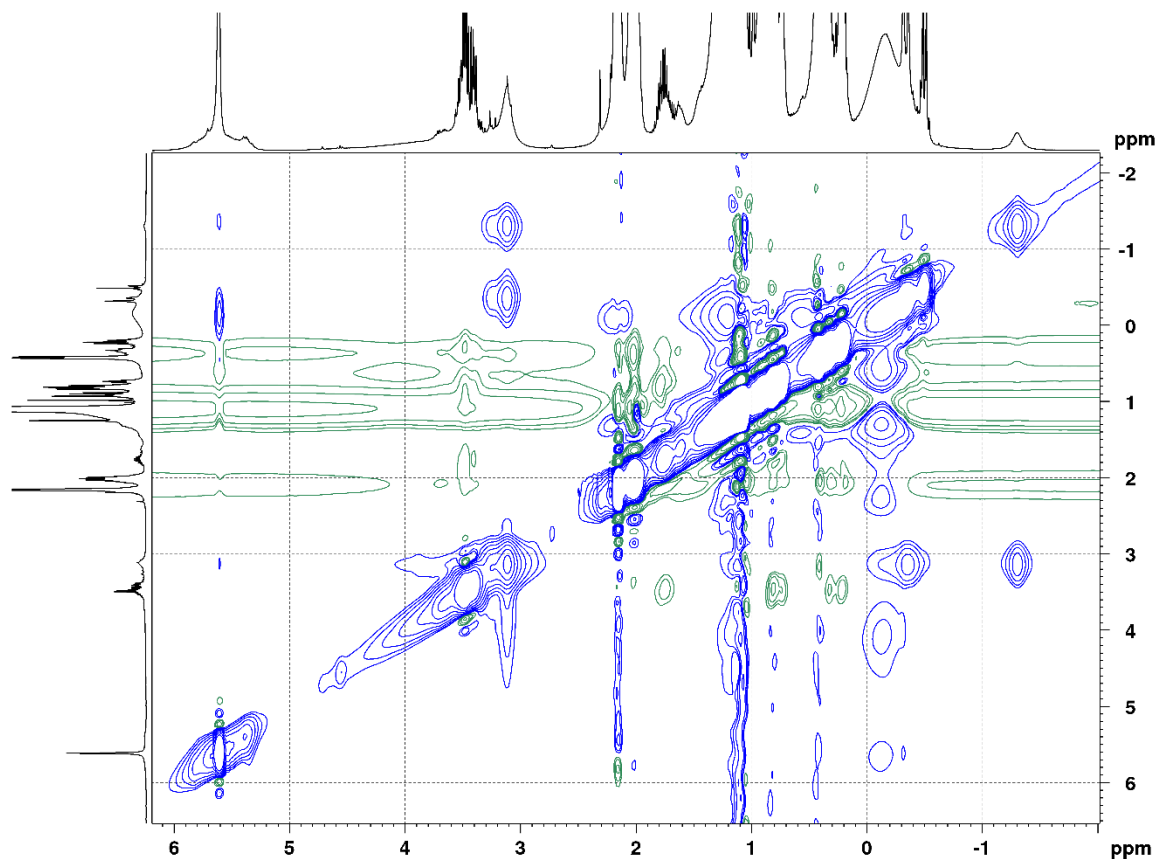


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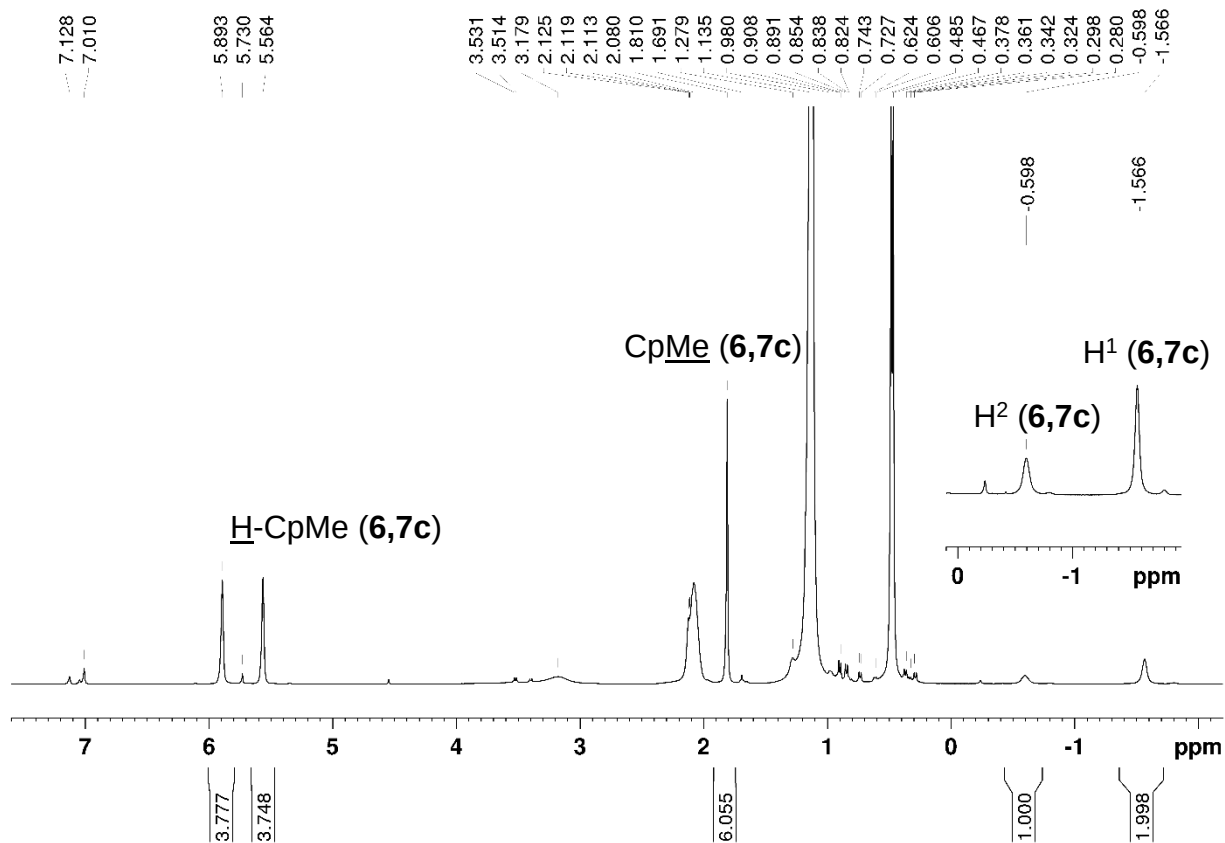


Figure S11. ^{13}C NMR of system $(\text{CpMe})_2\text{ZrCl}_2$ (**1c**) – HAlBu^i_2 (1:4) in C_7D_8 (298 K).

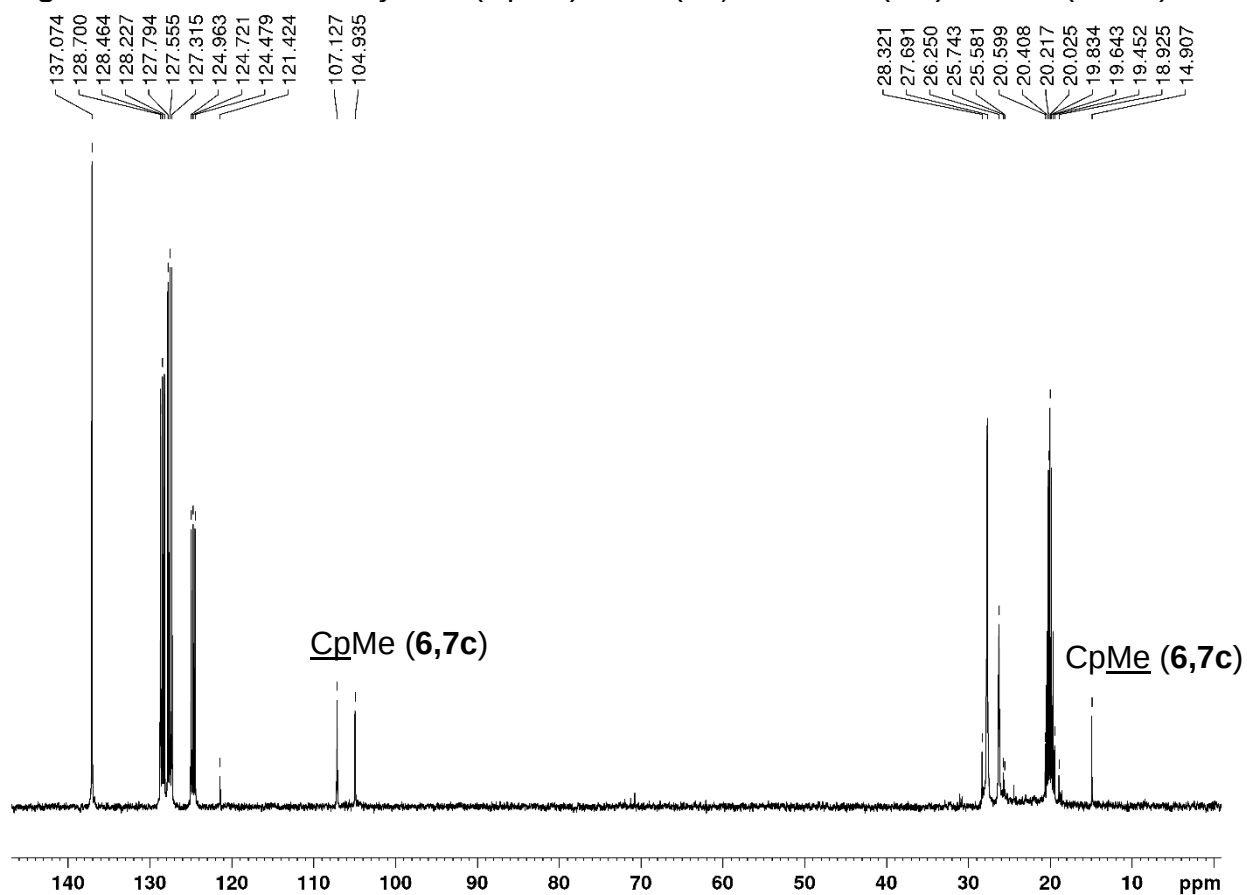


Figure S12. NOESY of system $(\text{CpMe})_2\text{ZrCl}_2$ (**1c**) – HAlBu^i_2 (1:4) in C_7D_8 (298 K).

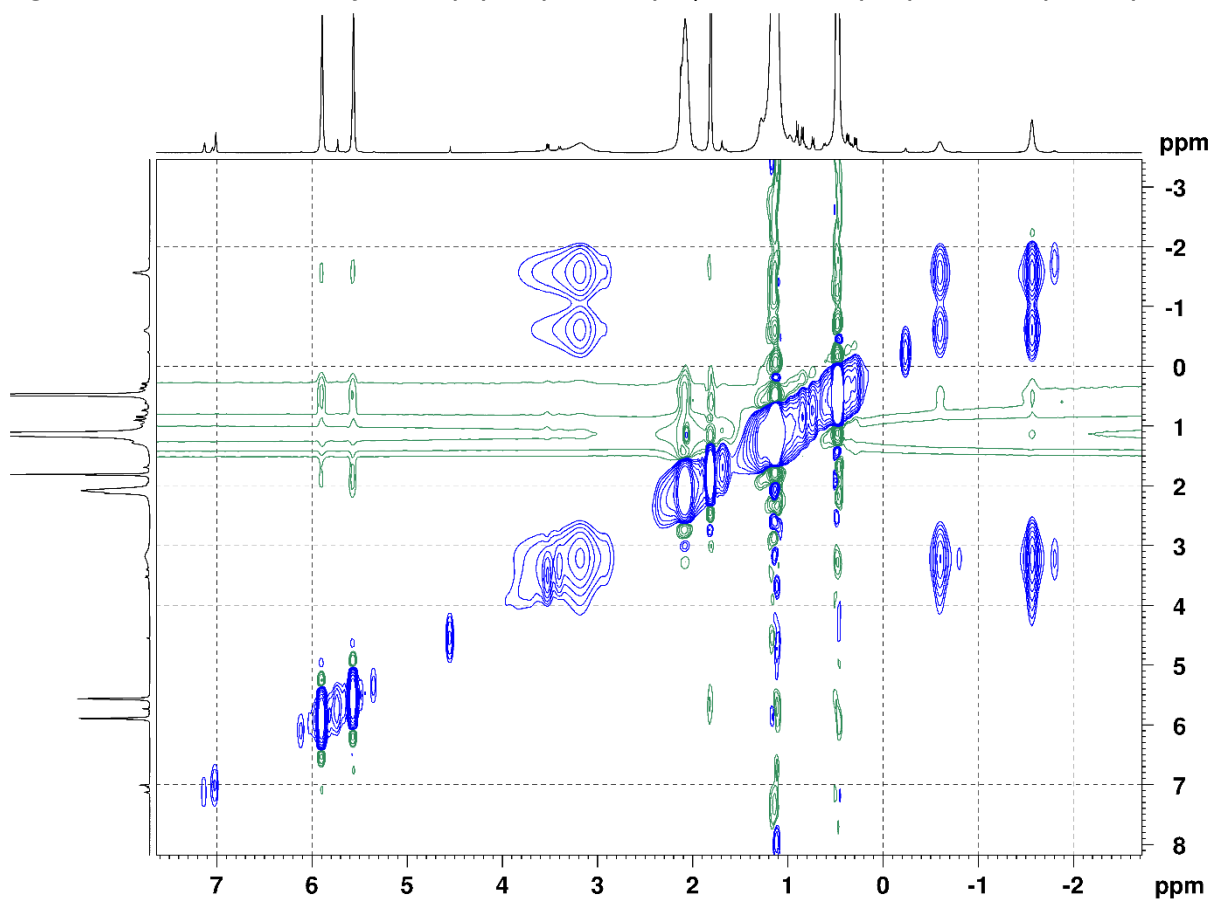


Figure S13. ^1H NMR of system $(\text{CpMe})_2\text{ZrCl}_2$ (**1c**) – HAlBu_2 (1:7) in C_7D_8 (298 K).

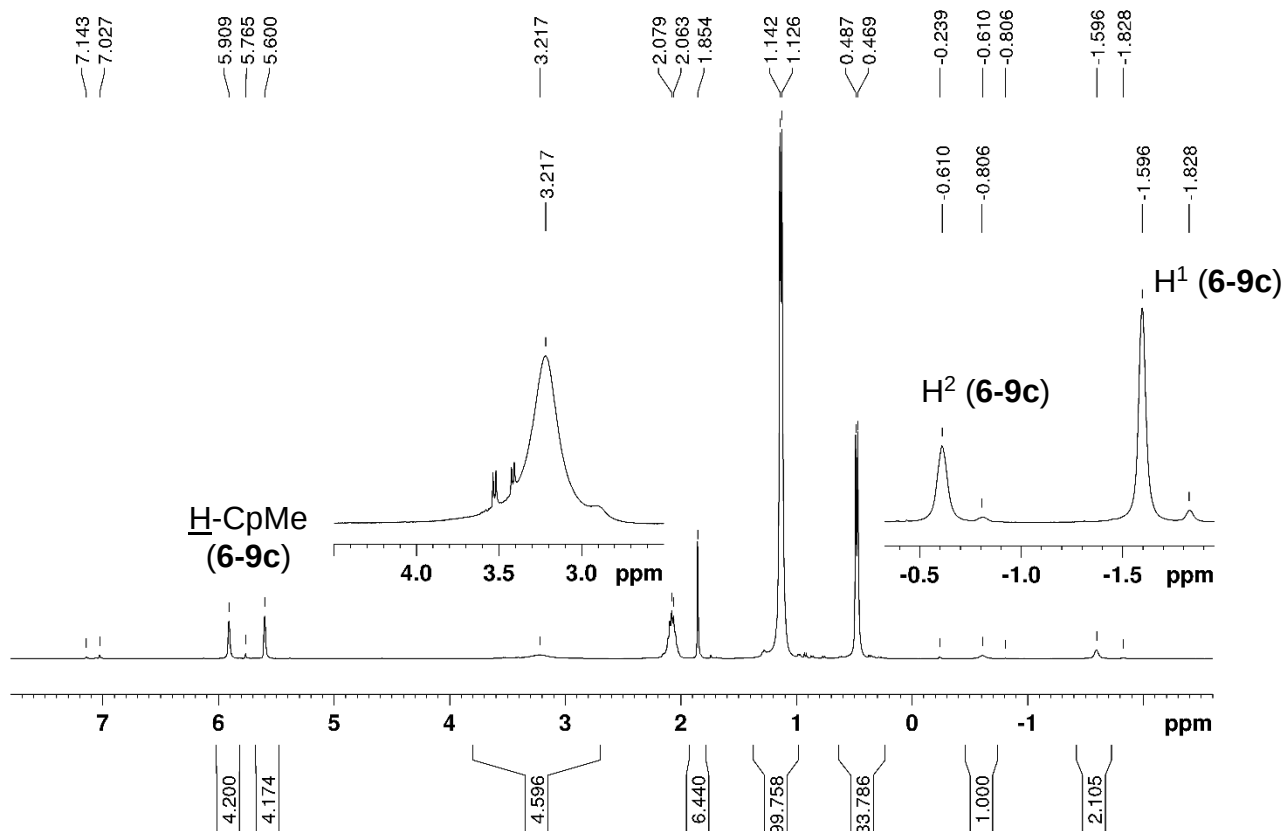


Figure S14. ^1H NMR of system $(\text{CpMe})_2\text{ZrCl}_2$ (**1c**) – HAlBu_2 – MMAO-12 (1:7:6) in C_7D_8 (298 K).

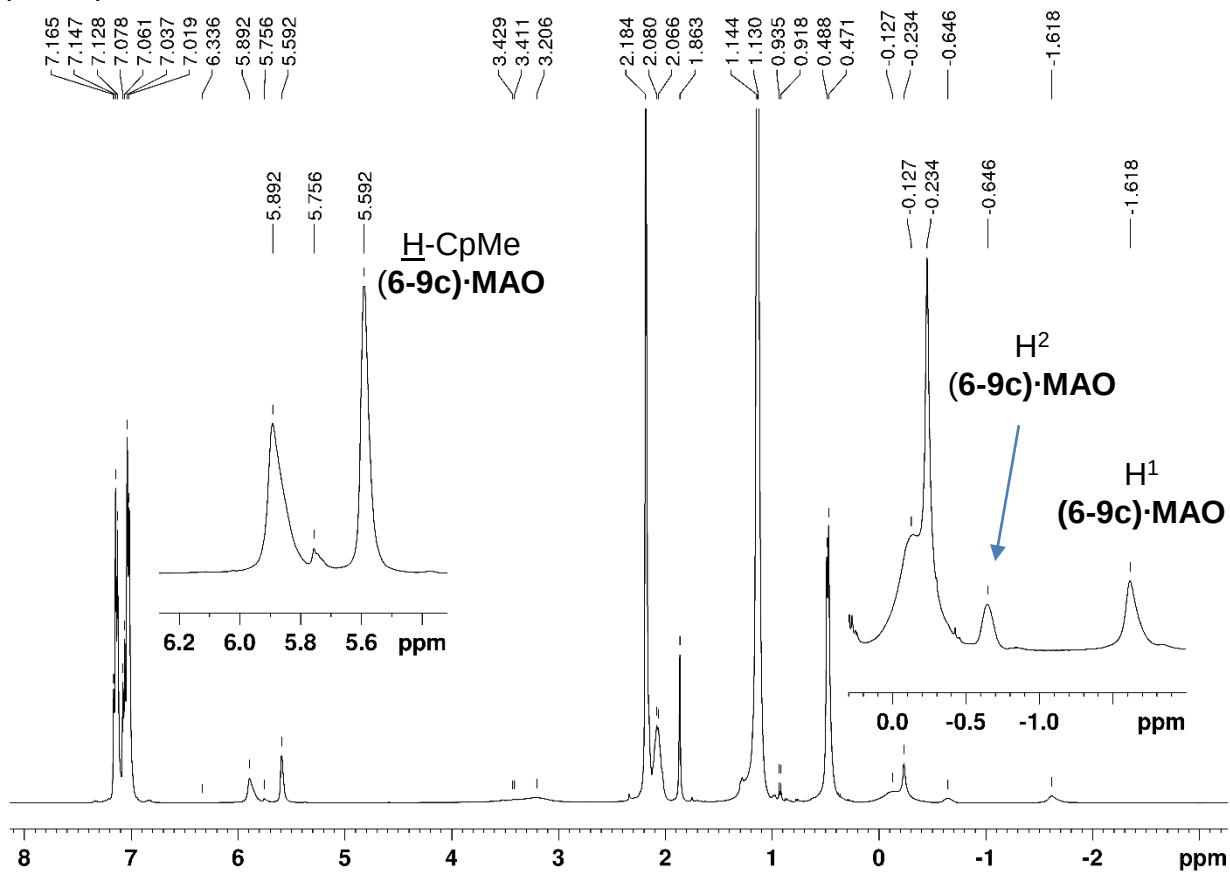


Figure S15. NOESY of system $(\text{CpMe})_2\text{ZrCl}_2$ (**1c**) – HAlBu_2 – MMAO-12 (1:7:6) in C_7D_8 (298 K).

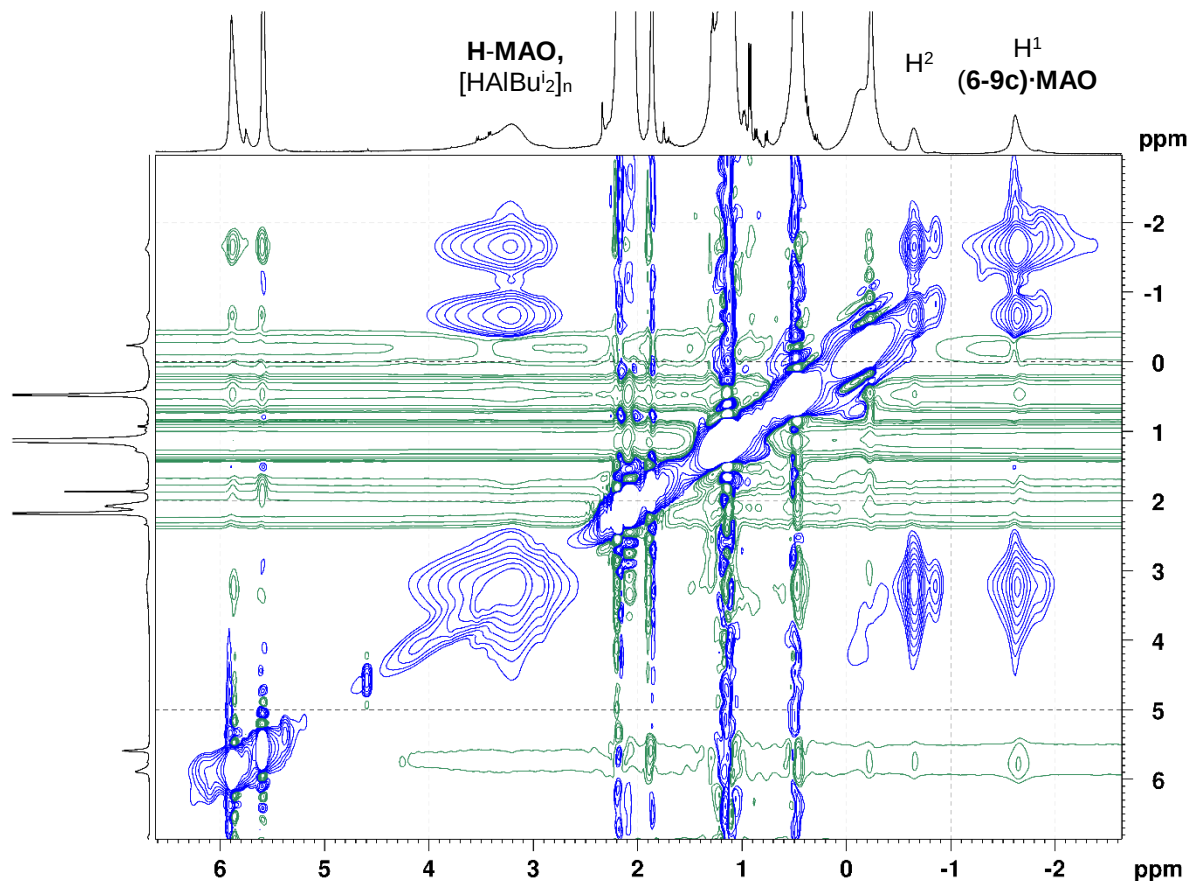


Figure S16. ^1H NMR of system $(\text{CpMe})_2\text{ZrCl}_2$ (**1c**) – HAlBu_2 – MMAO-12 (1:4:11) in C_7D_8 (298 K), reaction time – 6 h.

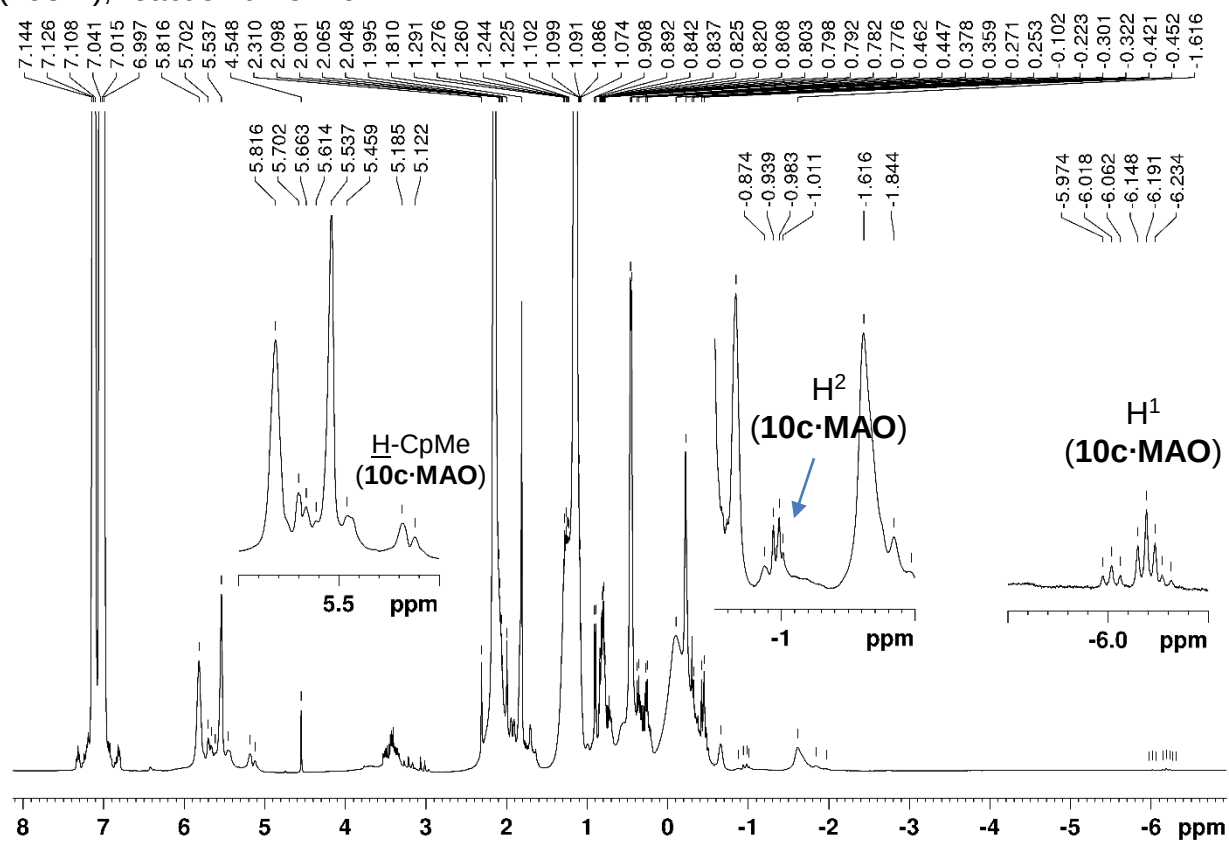


Figure S17. COSY HH of system $(\text{CpMe})_2\text{ZrCl}_2$ (**1c**) – HAlBu_2 – MMAO-12 (1:4:11) in C_7D_8 (298 K), reaction time – 6 h.

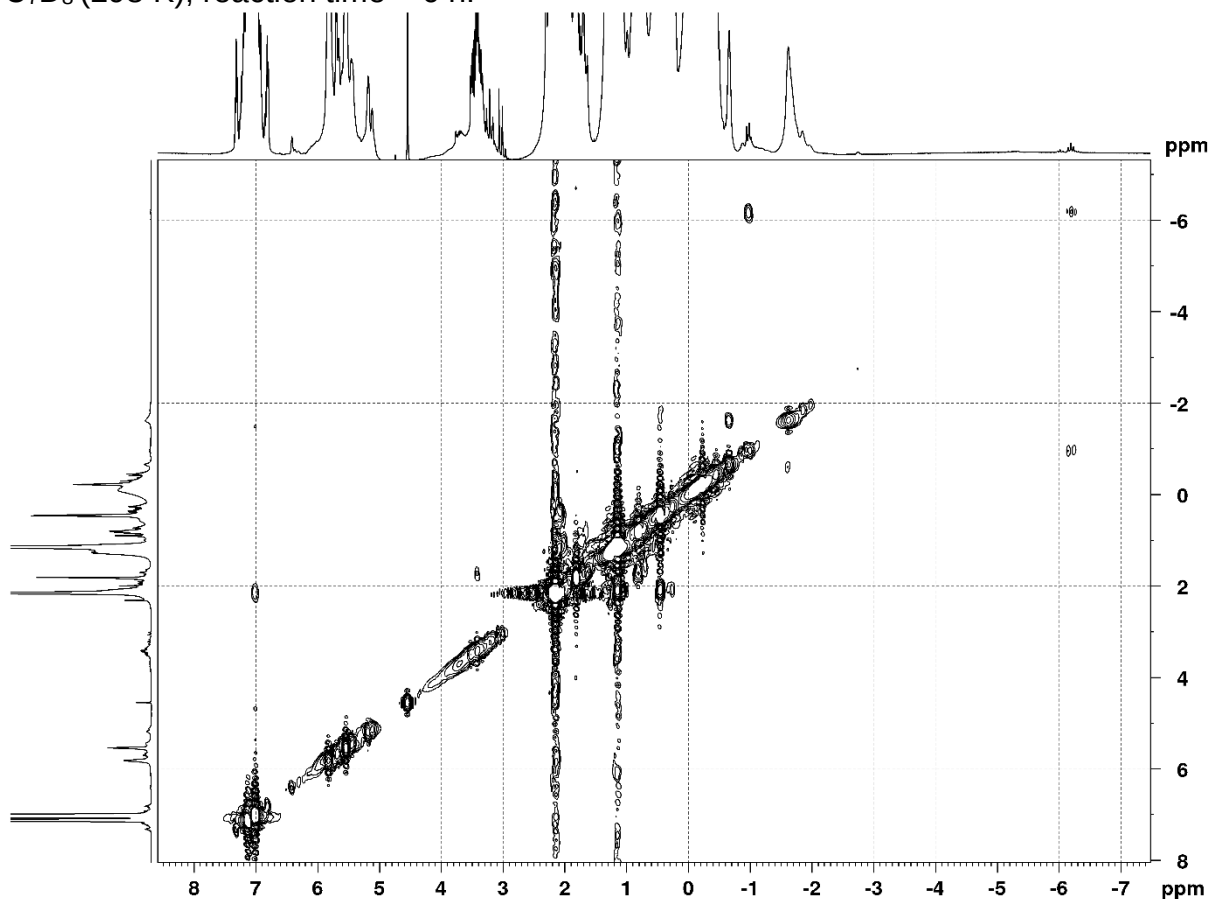


Figure S18. ^1H NMR of system *ansa*- $\text{Me}_4\text{C}_2\text{Cp}_2\text{ZrCl}_2$ (**1d**) – HAlBu_2 (1:5) in C_7D_8 (298 K).

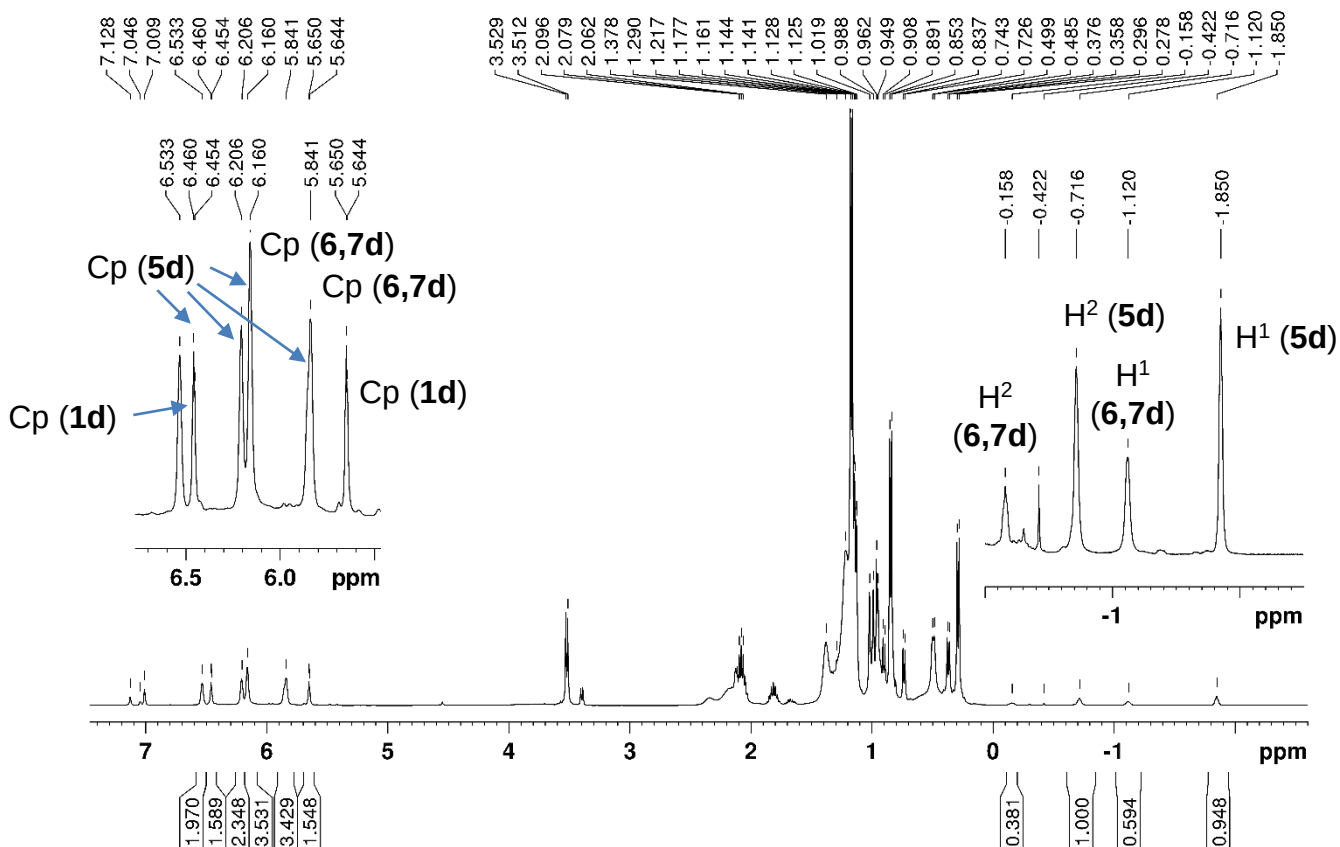


Figure S19. ^{13}C NMR of system *ansa*- $\text{Me}_4\text{C}_2\text{Cp}_2\text{ZrCl}_2$ (**1d**) – HAlBu^i_2 (1:5) in C_7D_8 (298 K).

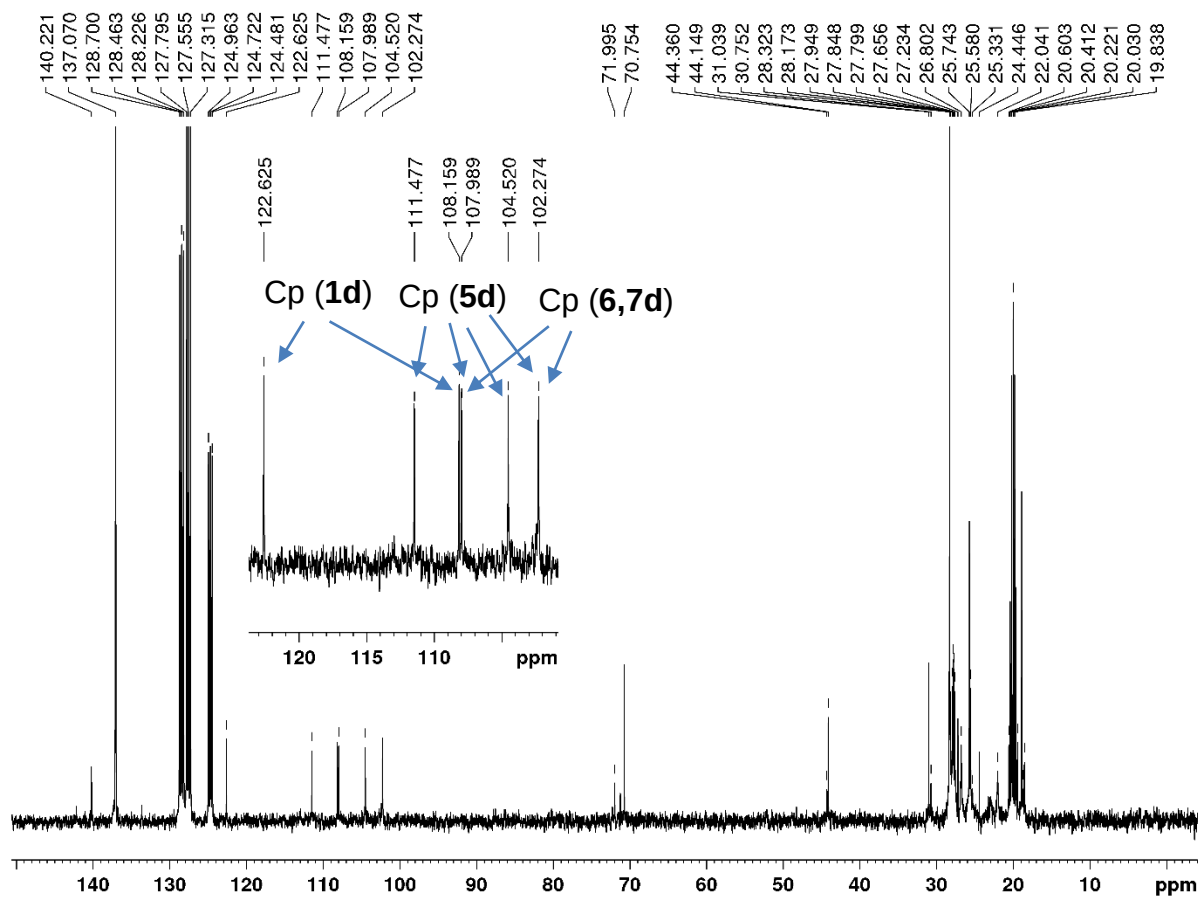


Figure S20. COSY HH of system *ansa*- $\text{Me}_4\text{C}_2\text{Cp}_2\text{ZrCl}_2$ (**1d**) – HAlBu^i_2 (1:5) in C_7D_8 (298 K).

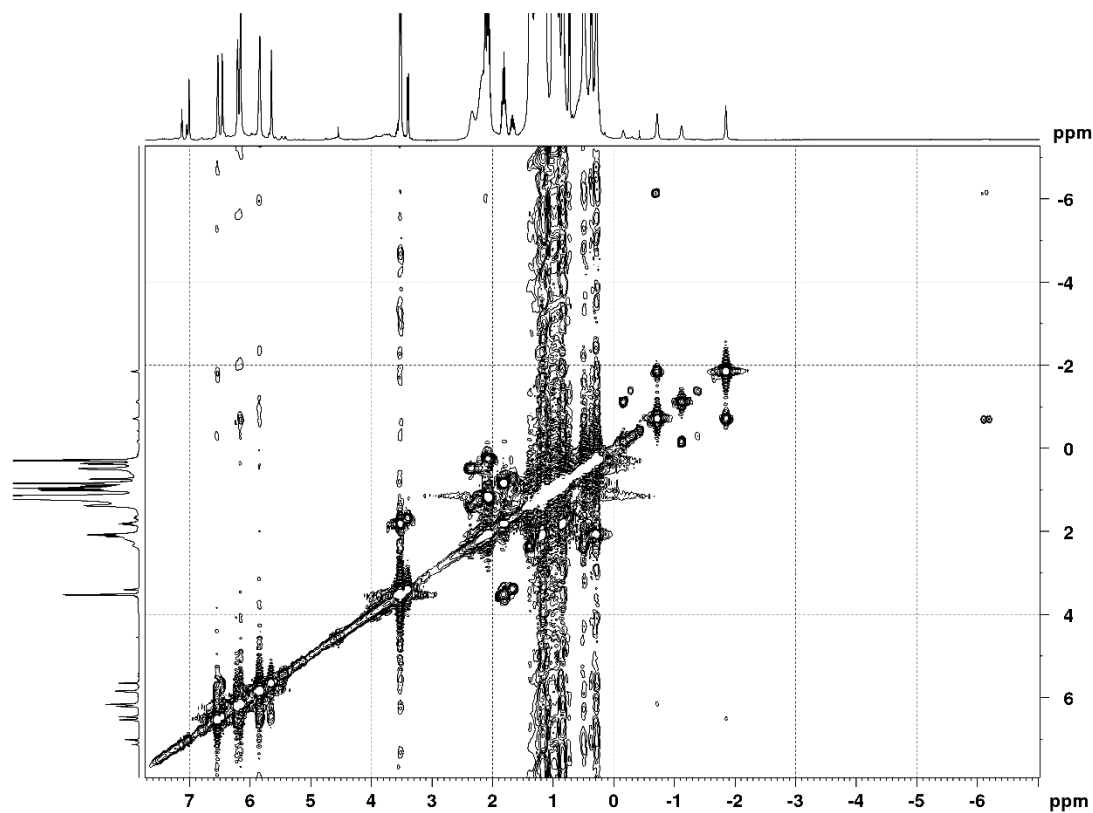


Figure S21. NOESY of system *ansa*-Me₄C₂Cp₂ZrCl₂ (**1d**) – HAlBu₂ (1:5) in C₇D₈ (298 K).

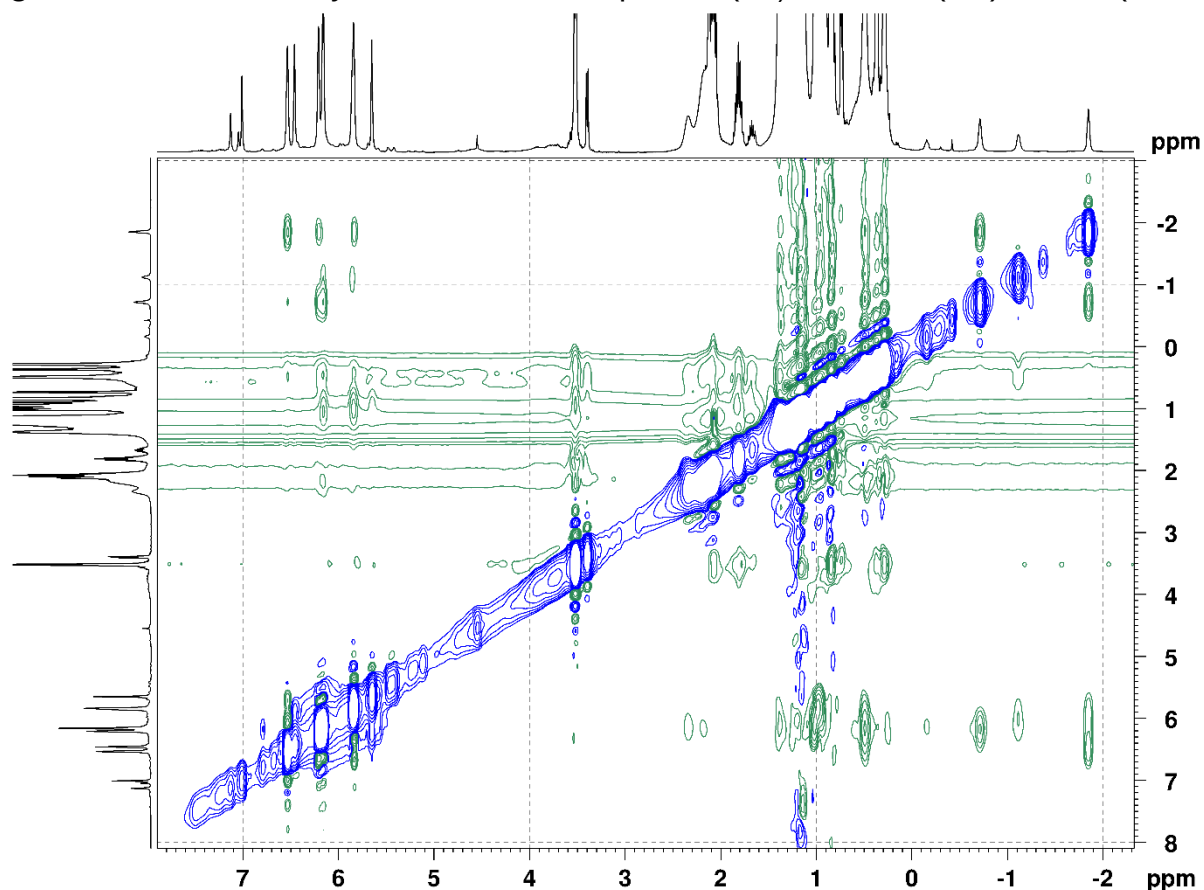


Figure S22. ¹H NMR of system *ansa*-Me₄C₂Cp₂ZrCl₂ (**1d**) – HAlBu₂ (1:8) in C₇D₈ (298 K).

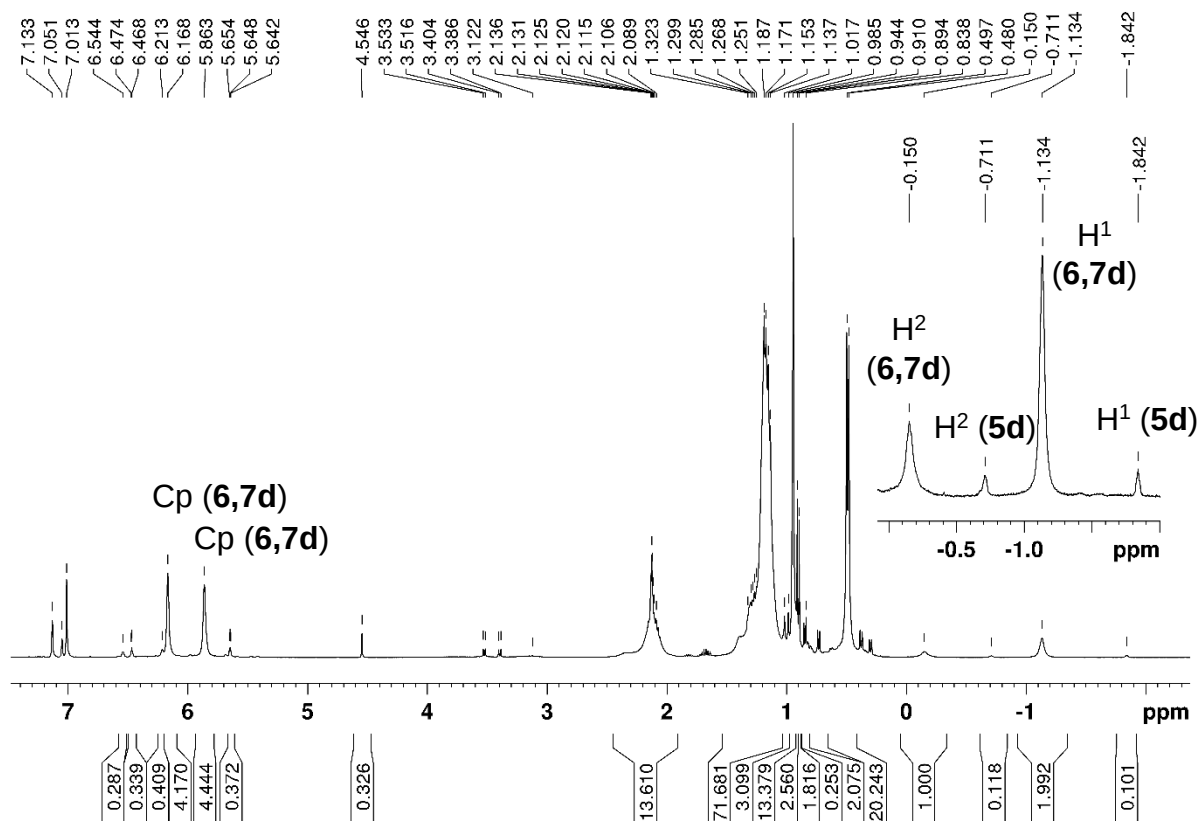


Figure S23. ^1H NMR of system *ansa*- $\text{Me}_4\text{C}_2\text{Cp}_2\text{ZrCl}_2$ (**1d**) – HAlBu^i_2 (1:14) in C_7D_8 (298 K).

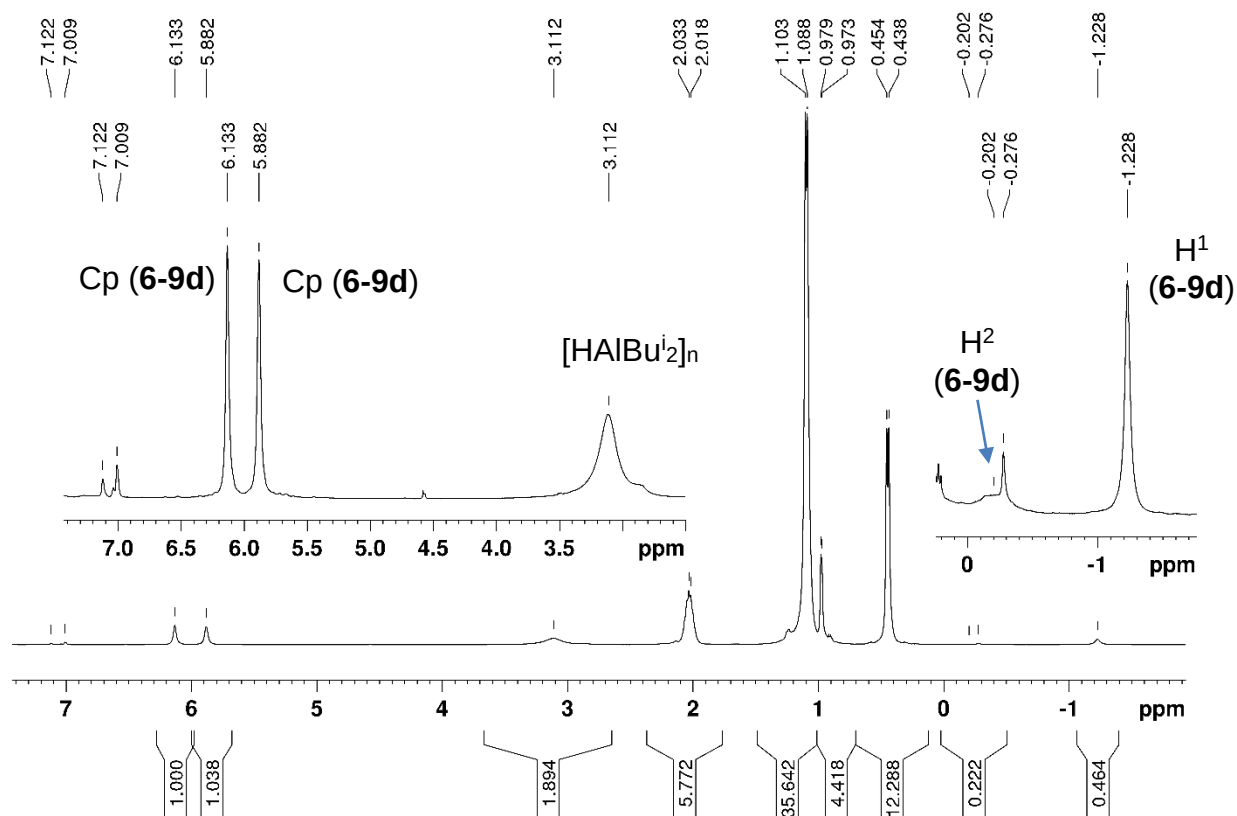


Figure S24. NOESY of system *ansa*- $\text{Me}_4\text{C}_2\text{Cp}_2\text{ZrCl}_2$ (**1d**) – HAlBu^i_2 (1:14) in C_7D_8 (298 K).

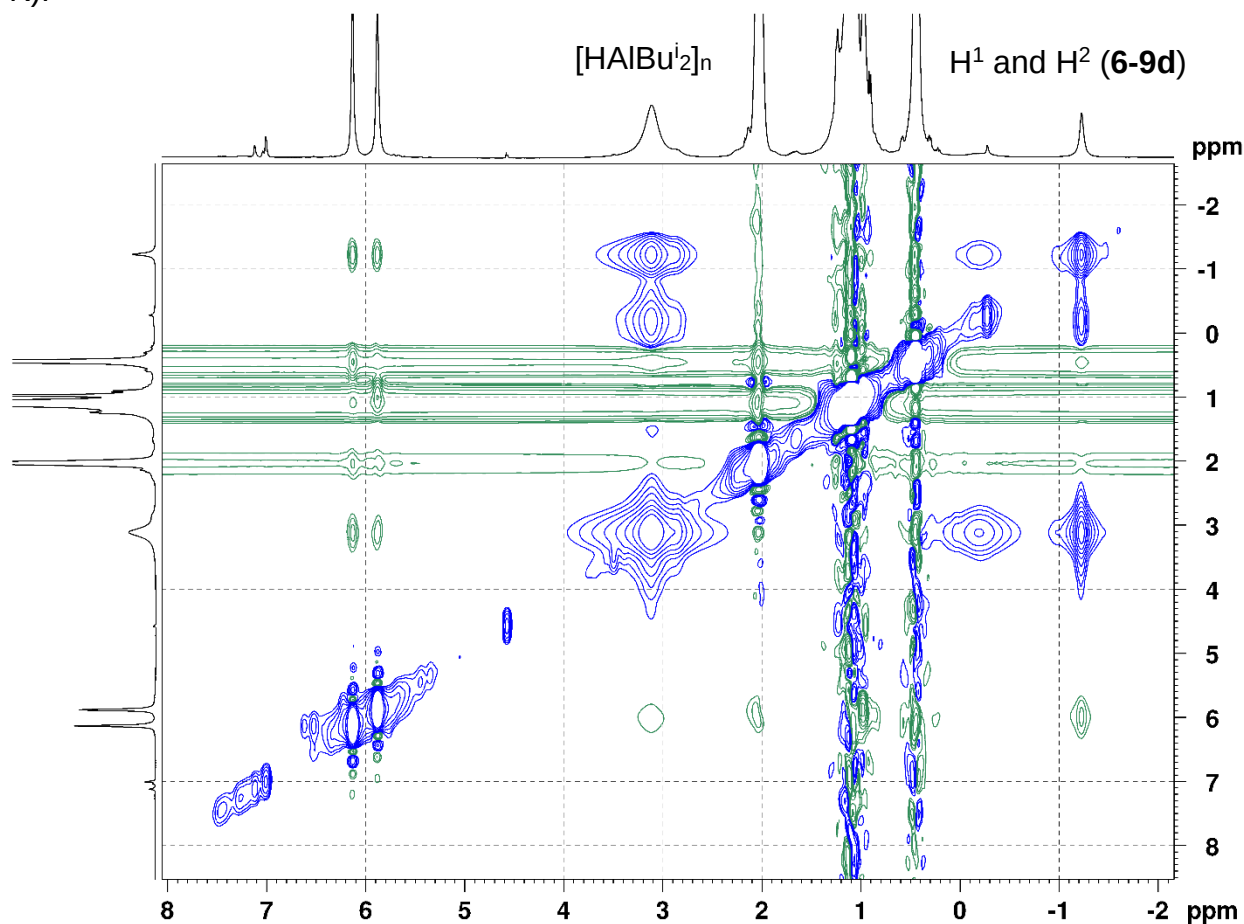


Figure S25. ^1H NMR of system *ansa*- $\text{Me}_4\text{C}_2\text{Cp}_2\text{ZrCl}_2$ (**1d**) – HAlBu^i_2 – MMAO-12 (1:5:14) in C_7D_8 (298 K).

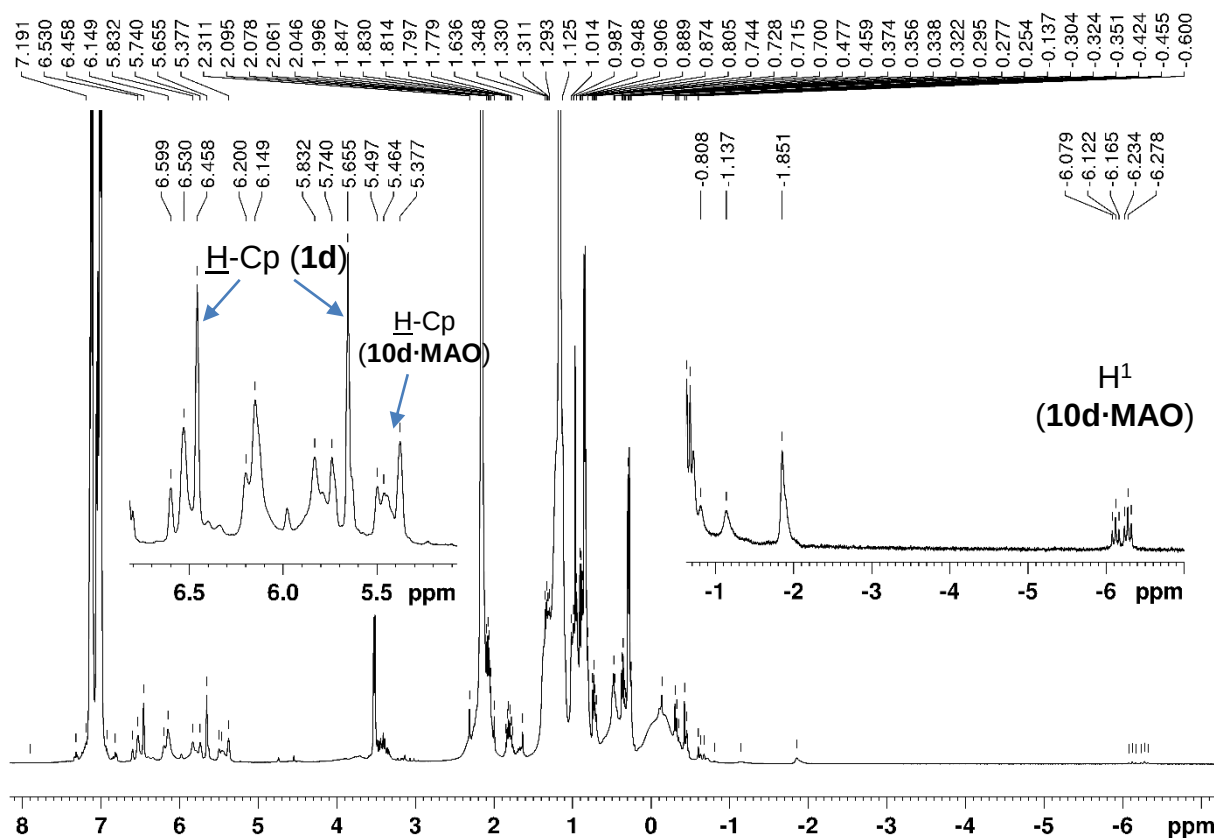


Figure S26. COSY HH of system *ansa*- $\text{Me}_4\text{C}_2\text{Cp}_2\text{ZrCl}_2$ (**1d**) – HAlBu^i_2 – MMAO-12 (1:5:14) in C_7D_8 (298 K).

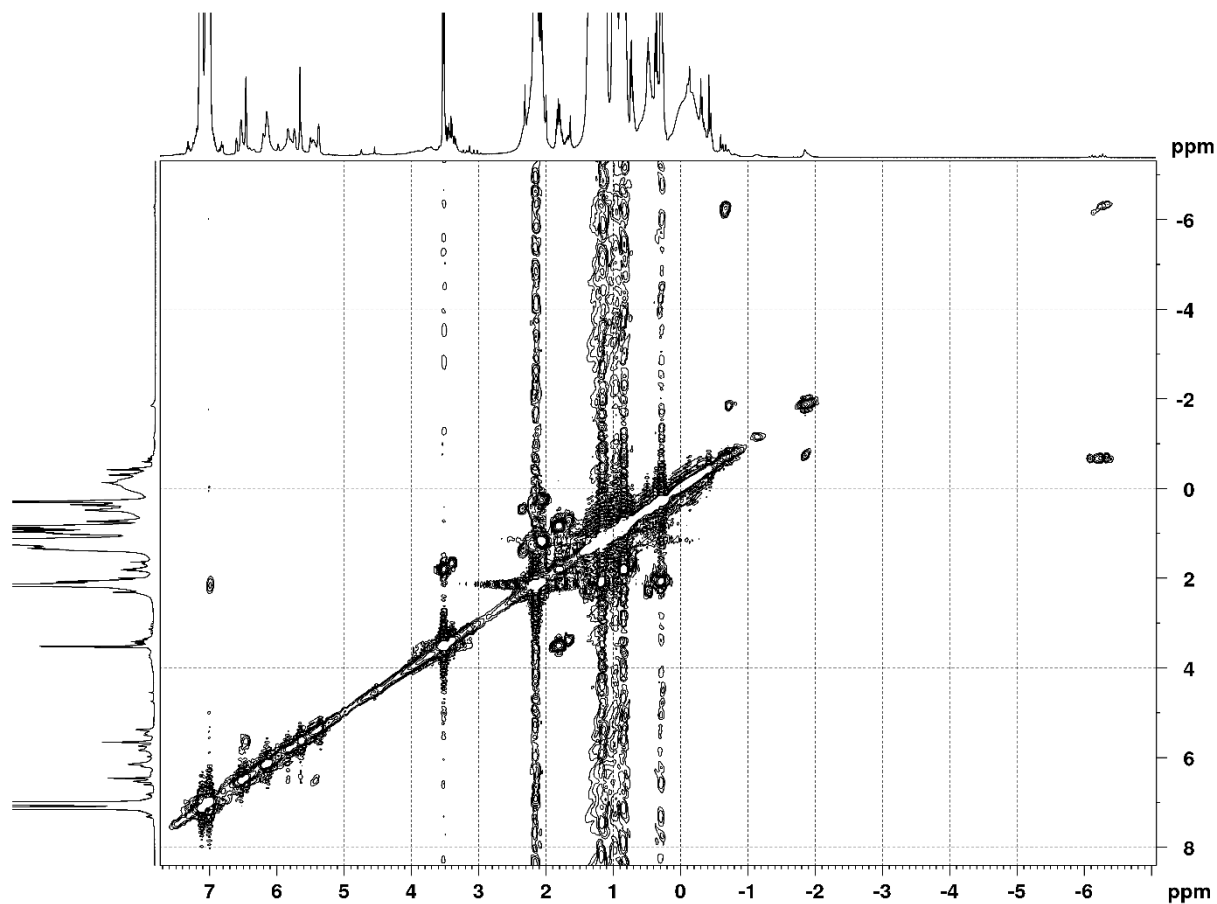


Figure S27. NOESY of system *ansa*-Me₄C₂Cp₂ZrCl₂ (**1d**) – HAIBu₂ – MMAO-12 (1:5:14) in C₇D₈ (298 K).

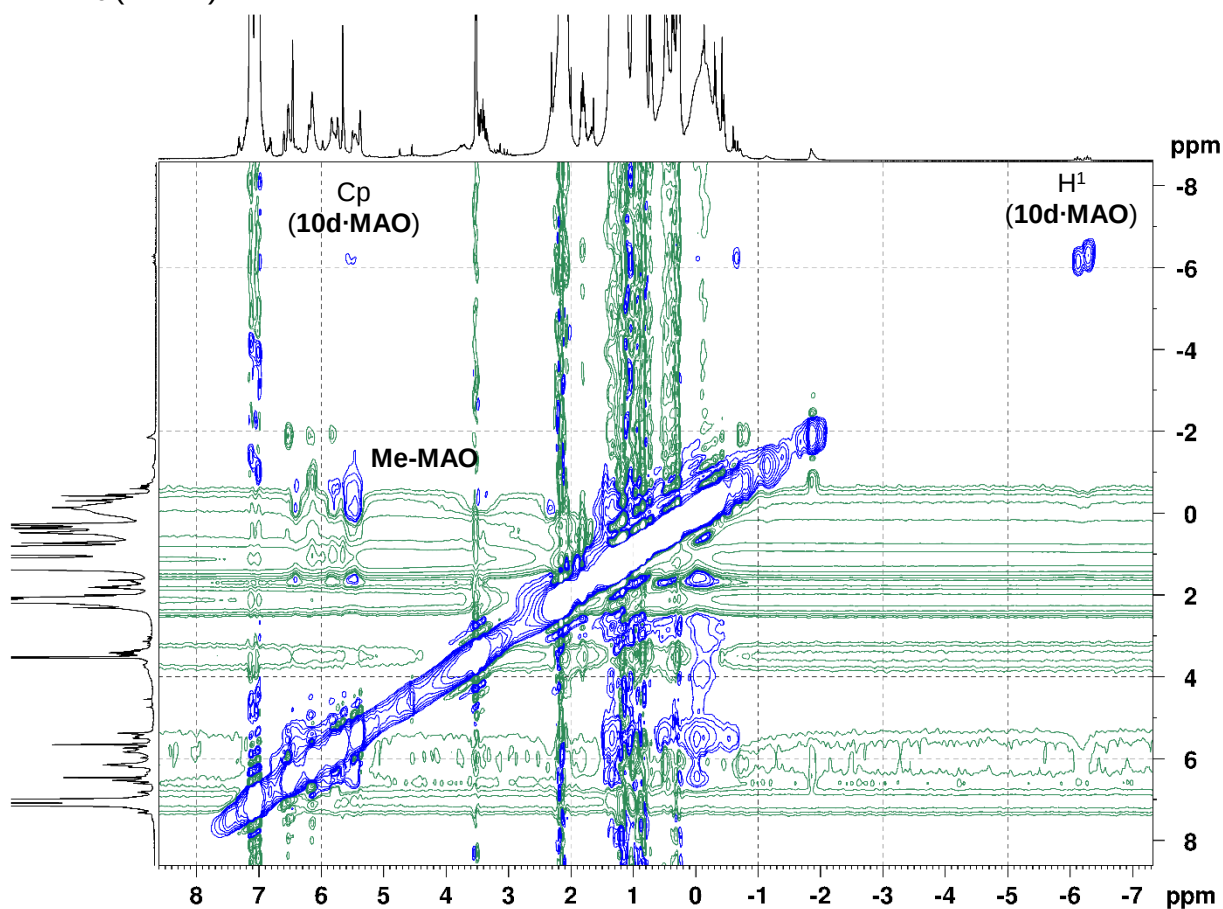


Figure S28. ¹H NMR of system *ansa*-Me₄C₂Cp₂ZrCl₂ (**1d**) – HAIBu₂ (1:2) in CDCl₃ (298 K).

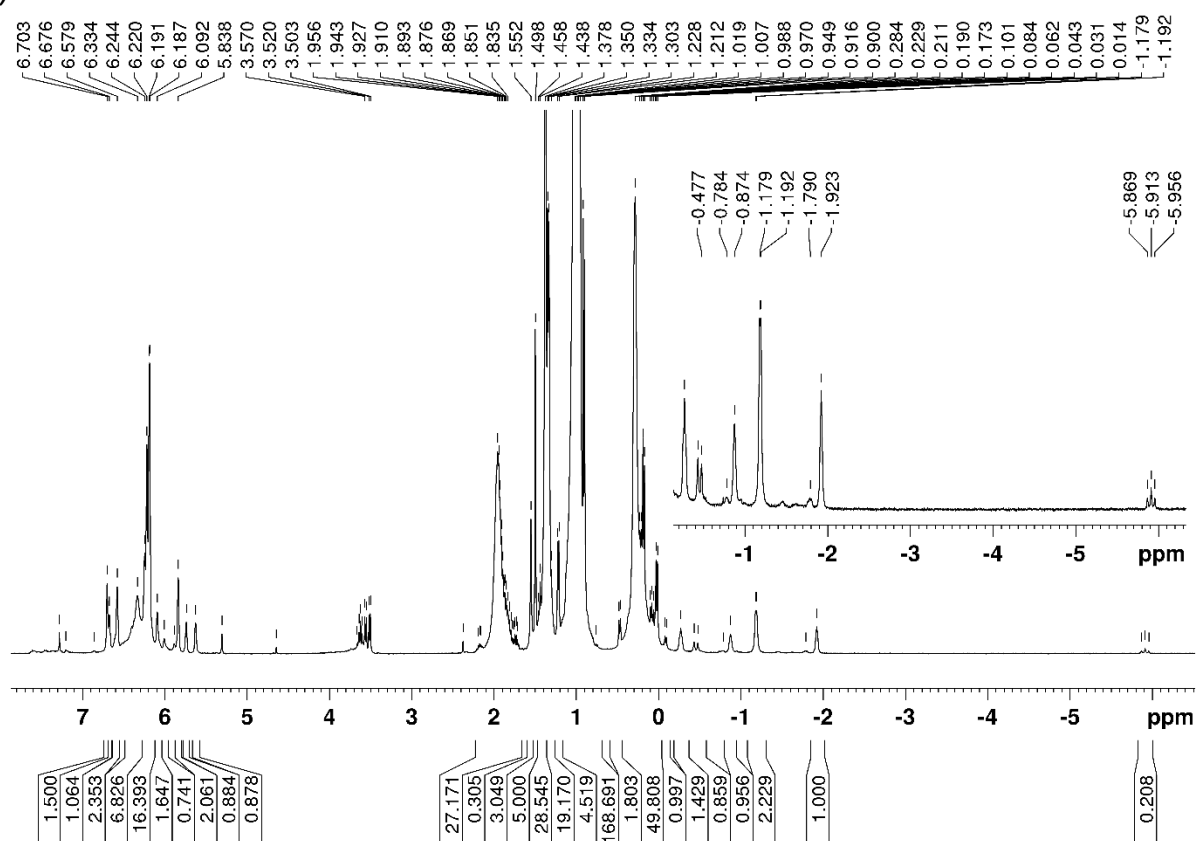


Figure S29. ^1H NMR of system *ansa*- $\text{Me}_4\text{C}_2\text{Cp}_2\text{ZrCl}_2$ (**1d**) – HAlBu_2 – MMAO-12 (1:2:3) in CDCl_3 (298 K).

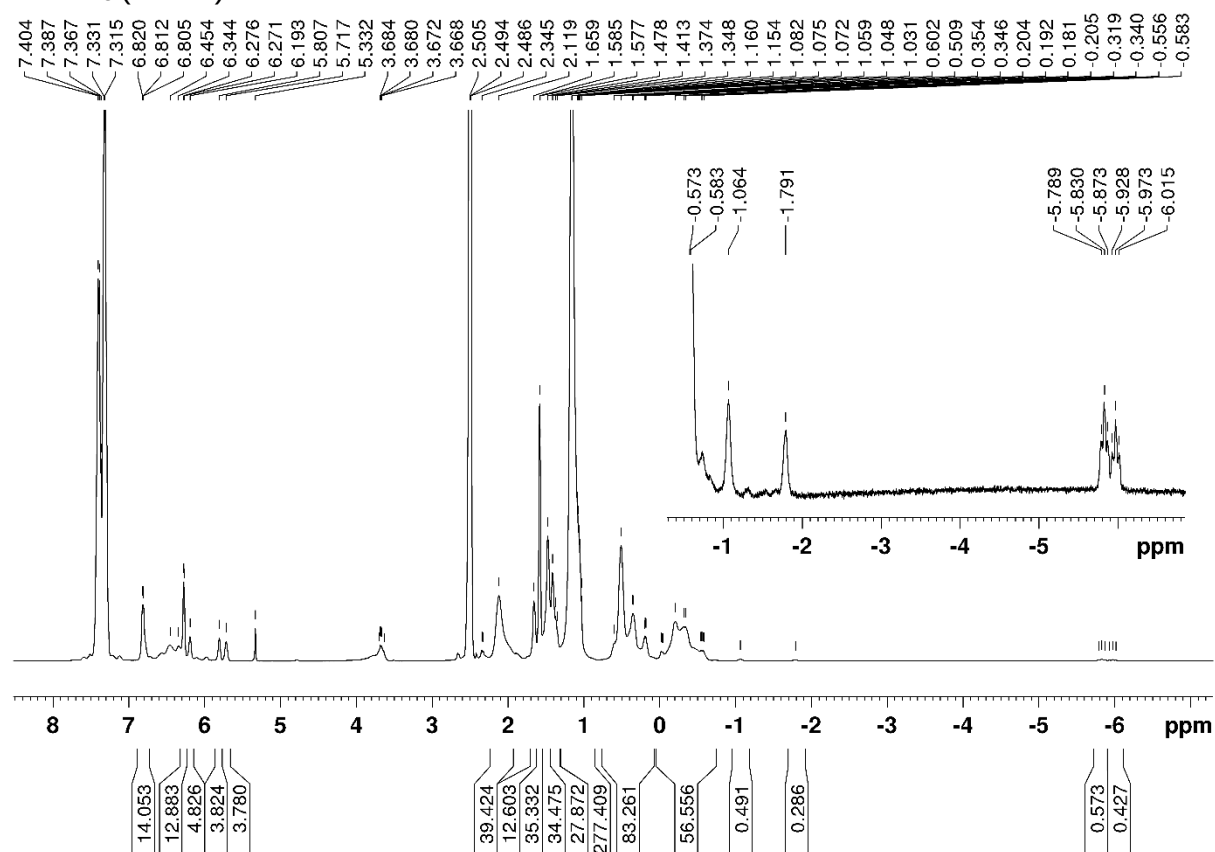


Figure S30. ^1H NMR of system *ansa*- $\text{Me}_4\text{C}_2\text{Cp}_2\text{ZrCl}_2$ (**1d**) – HAlBu_2 – MMAO-12 (1:14:8) in C_7D_8 (298 K).

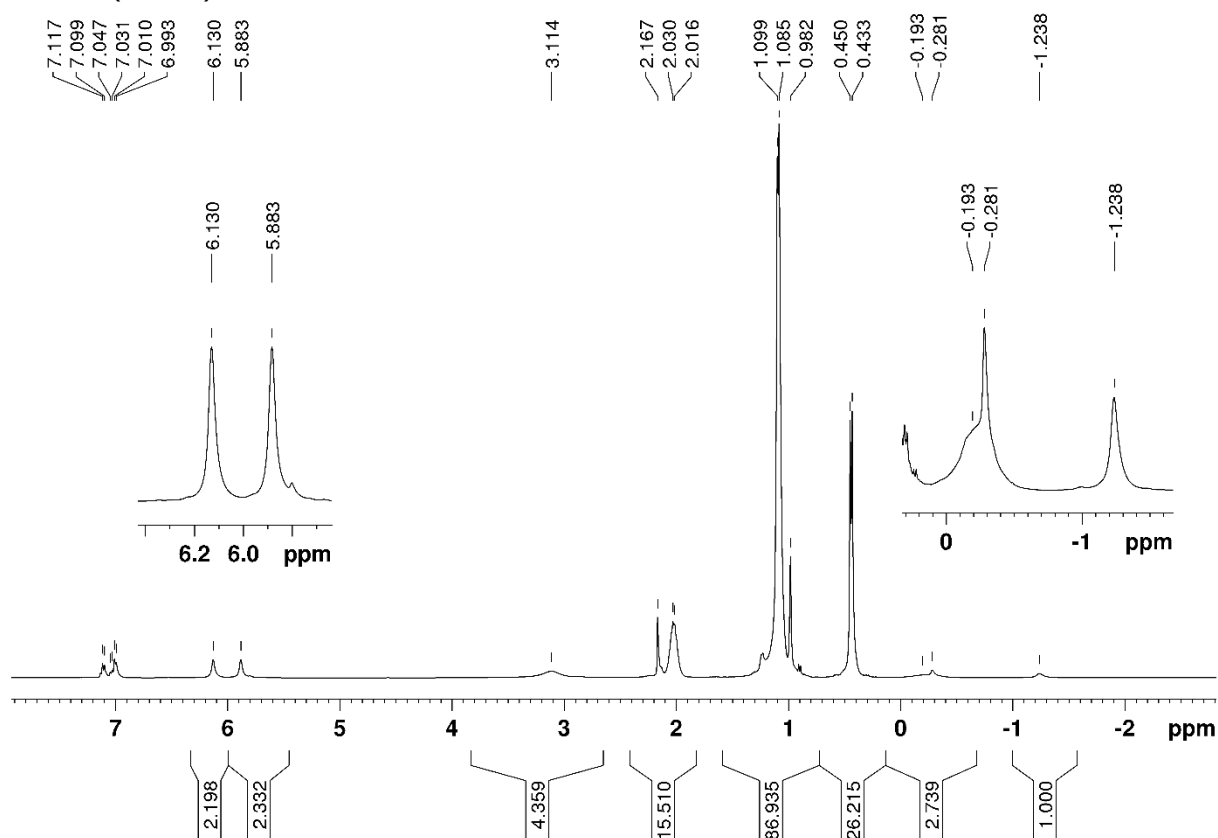


Figure S31. NOESY of system *ansa*-Me₄C₂Cp₂ZrCl₂ (**1d**) – HAIBu₂ – MMAO-12 (1:14:8) in C₇D₈ (298 K).

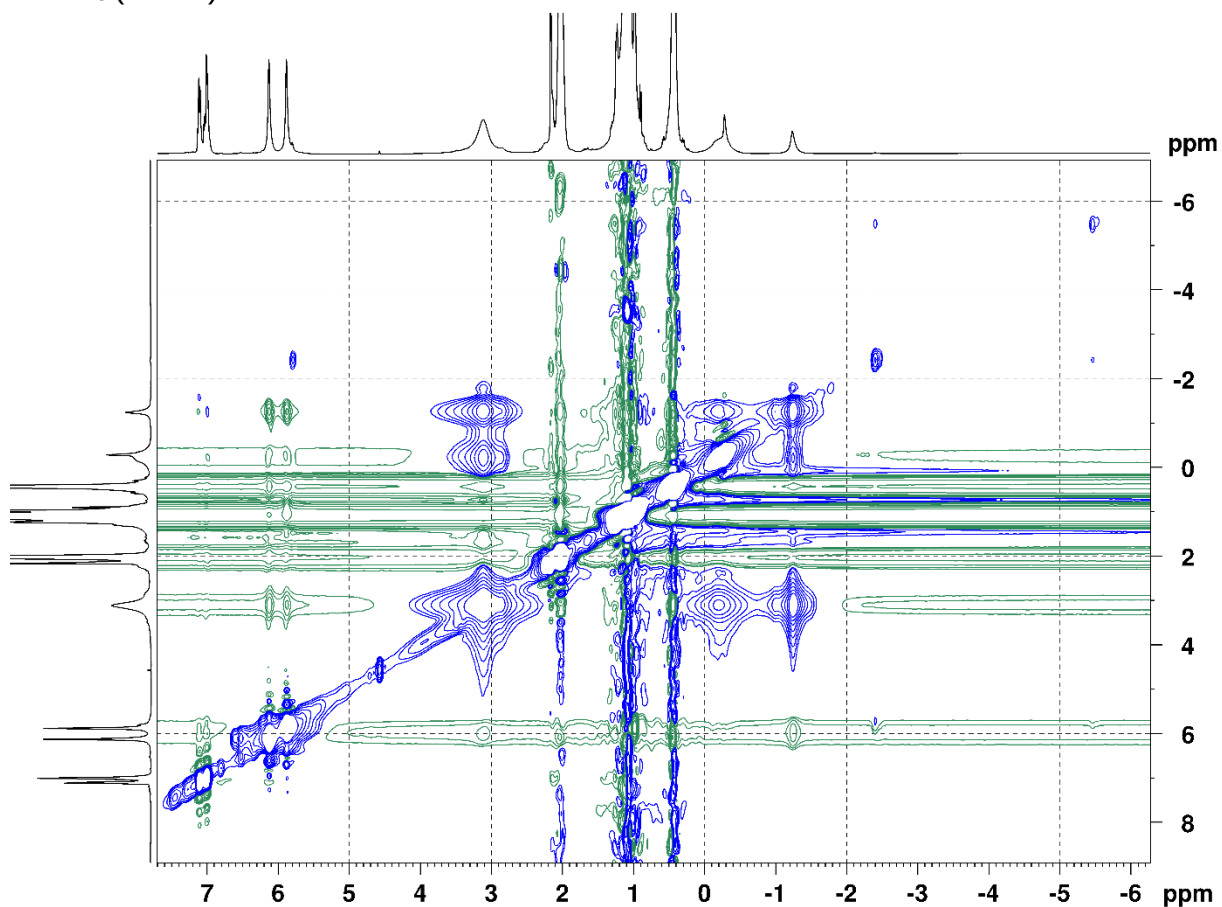


Figure S32. ¹H NMR of system Me₂CInd₂ZrCl₂ (**1e**) – HAIBu₂ (1:4) in C₇D₈ (298 K).

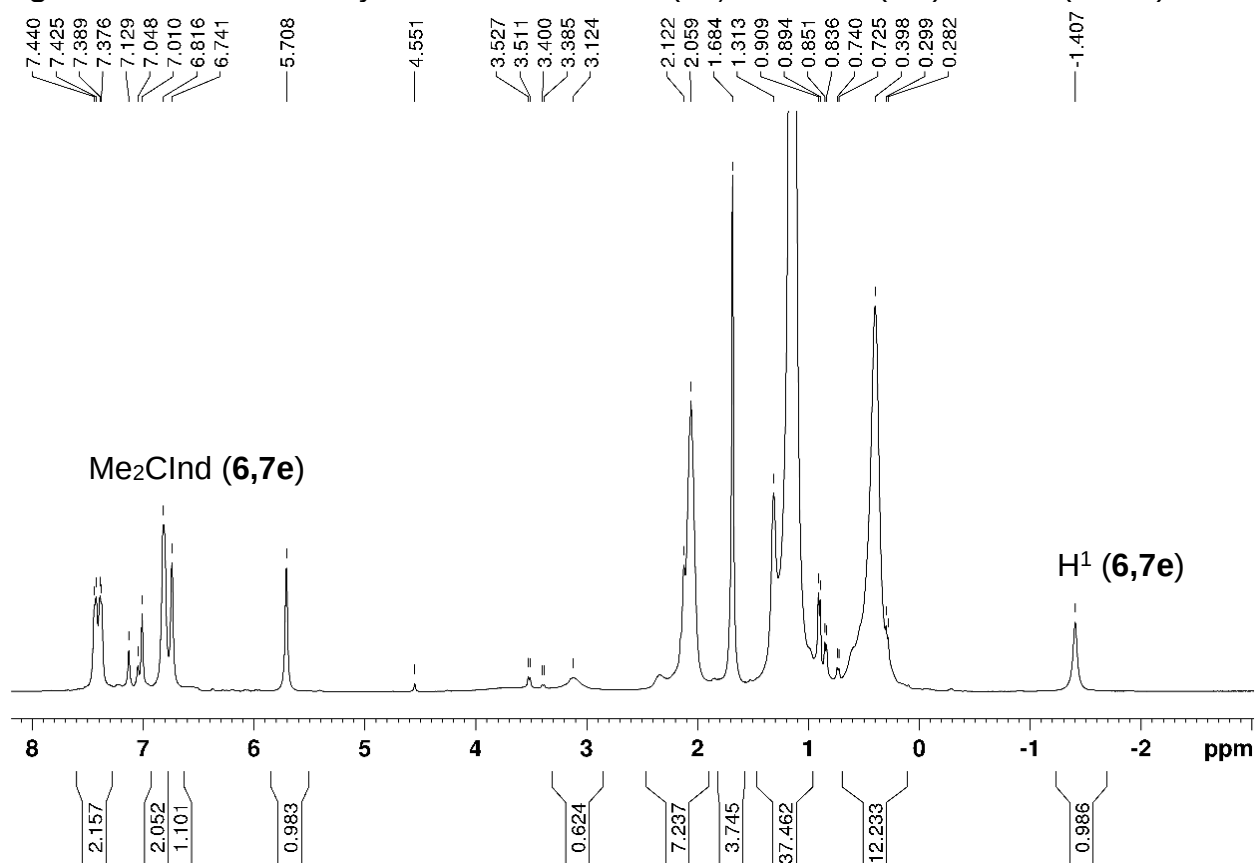


Figure S33. ^{13}C NMR of system $\text{Me}_2\text{CInd}_2\text{ZrCl}_2$ (**1e**) – HAlBu^i_2 (1:4) in C_7D_8 (298 K).

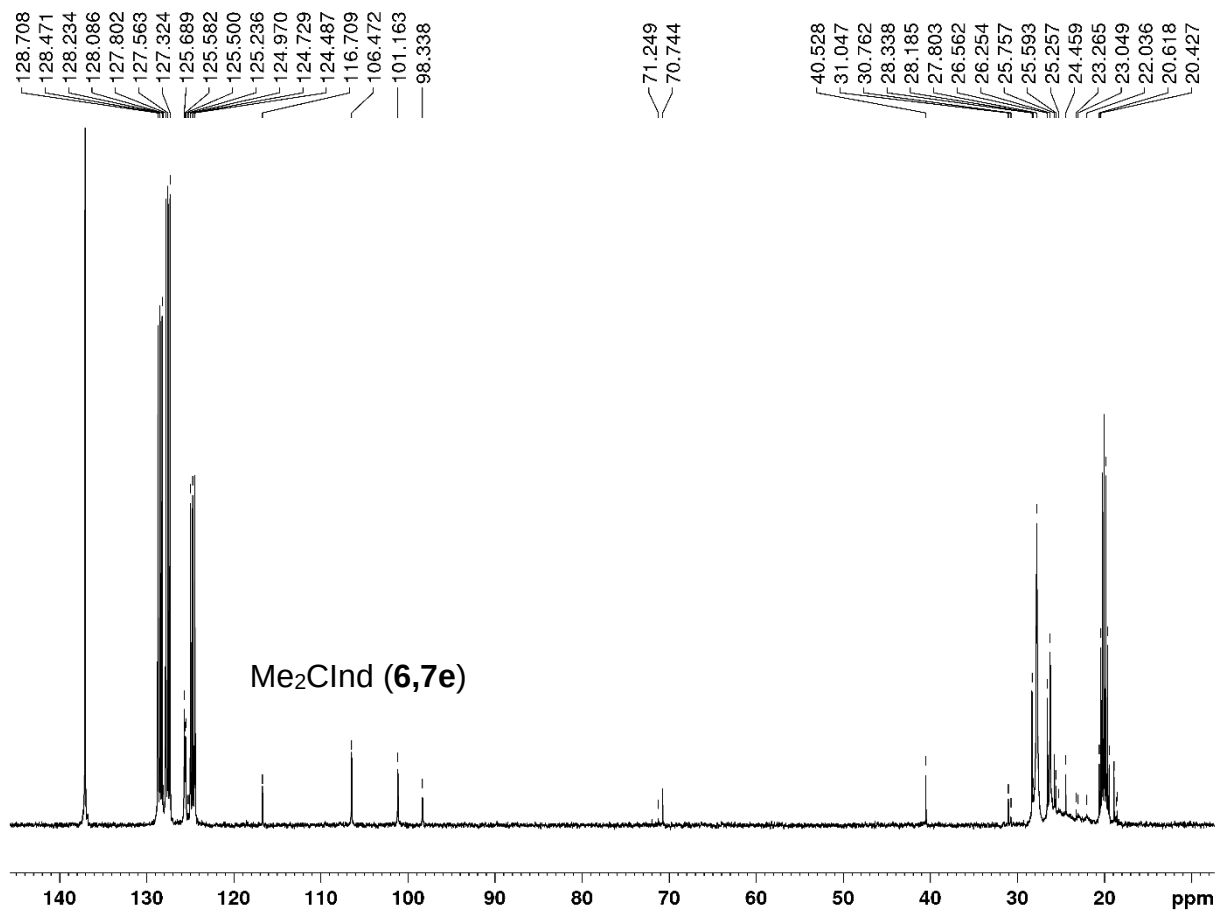


Figure S34. COSY HH of system $\text{Me}_2\text{CInd}_2\text{ZrCl}_2$ (**1f**) – HAlBu^i_2 (1:4) in C_7D_8 (280 K).

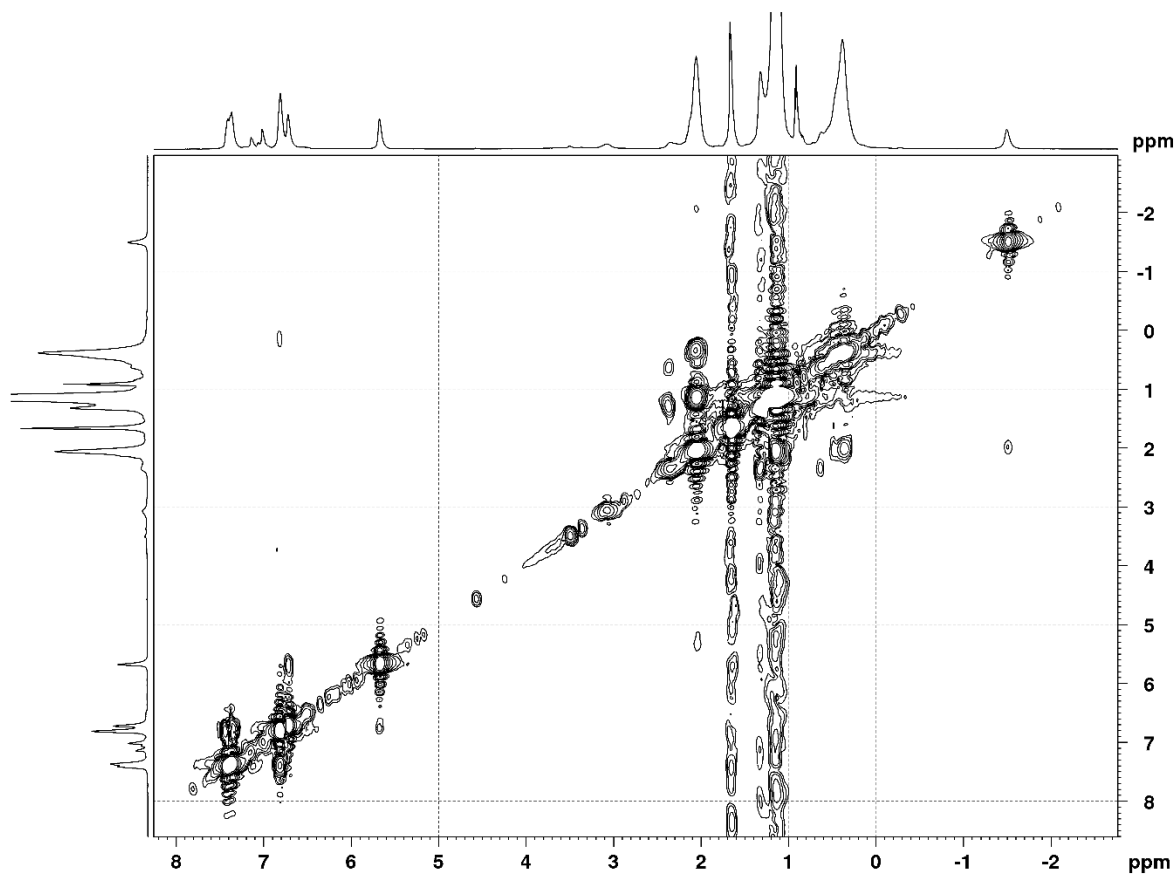


Figure S35. NOESY of system $\text{Me}_2\text{CInd}_2\text{ZrCl}_2$ (**1e**) – HAlBu_2 (1:4) in C_7D_8 (298 K).

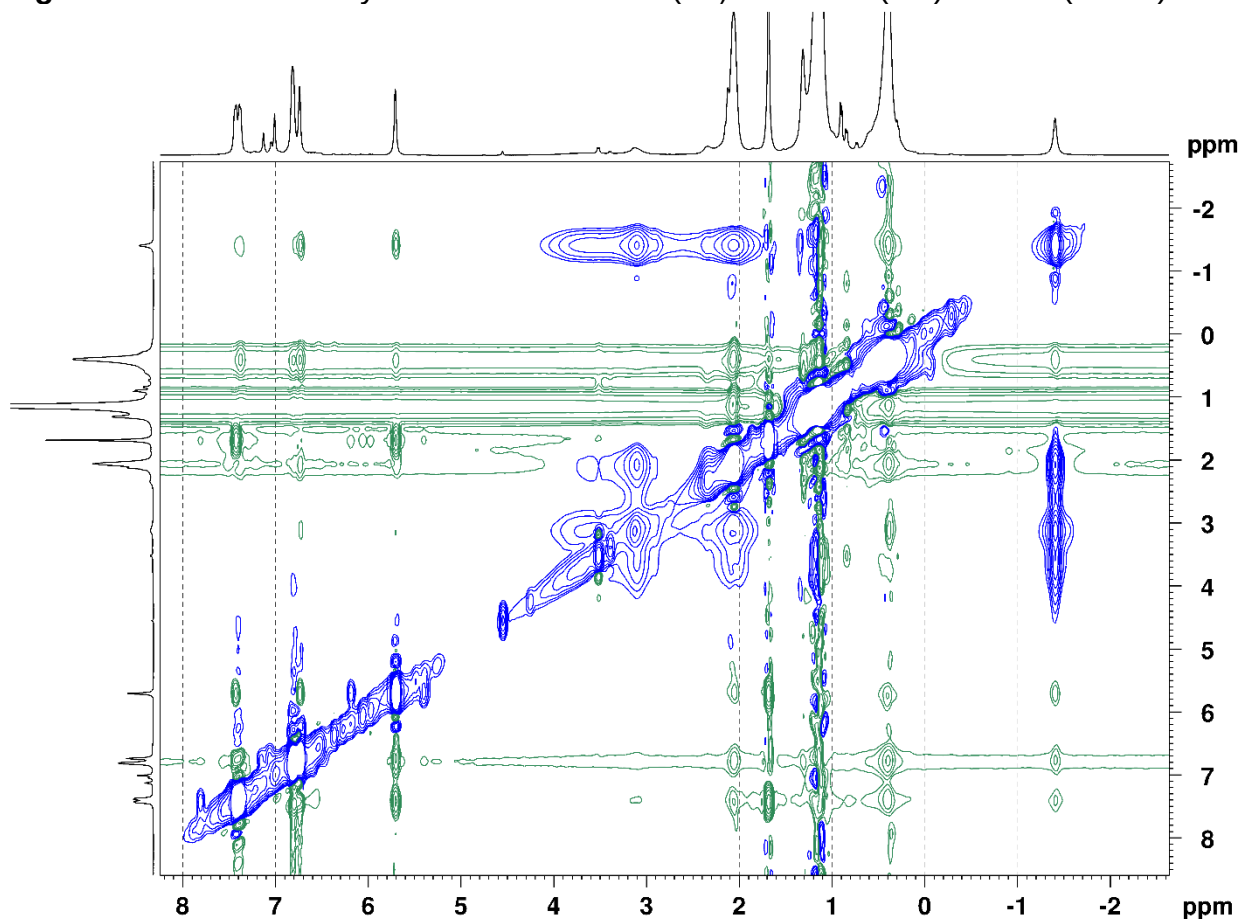


Figure S36. ^1H NMR of system $\text{Me}_2\text{CInd}_2\text{ZrCl}_2$ (**1e**) – HAlBu_2 – MMAO-12 (1:4:8) in C_7D_8 (298 K).

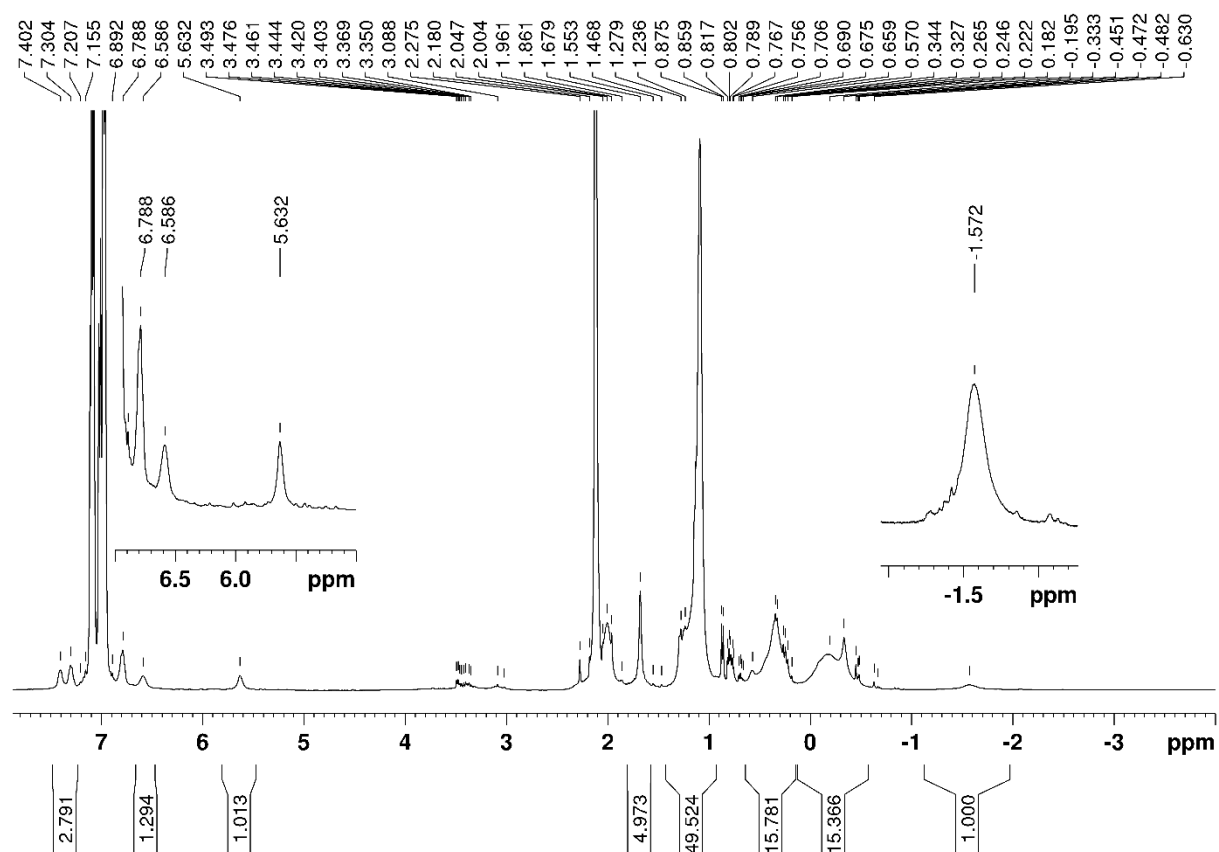


Figure S37. NOESY of system $\text{Me}_2\text{CInd}_2\text{ZrCl}_2$ (**1e**) – HAlBu_2 – MMAO-12 (1:4:8) in C_7D_8 (298 K).

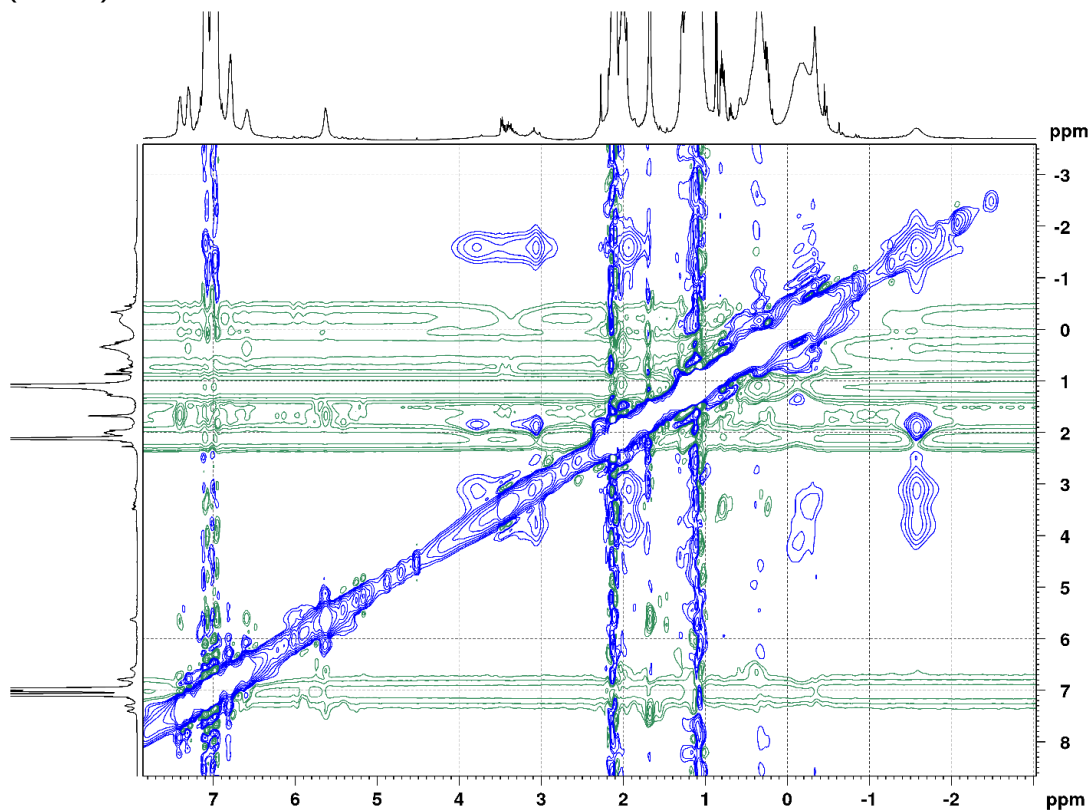


Figure S38. ^{13}C NMR of products obtained after the addition of hexene-1 to the system $(\text{CpMe})_2\text{ZrCl}_2$ (**1c**) – HAlBu_2 – MMAO-12 (1:4:11) in C_7D_8 , 333 K, 10 min.

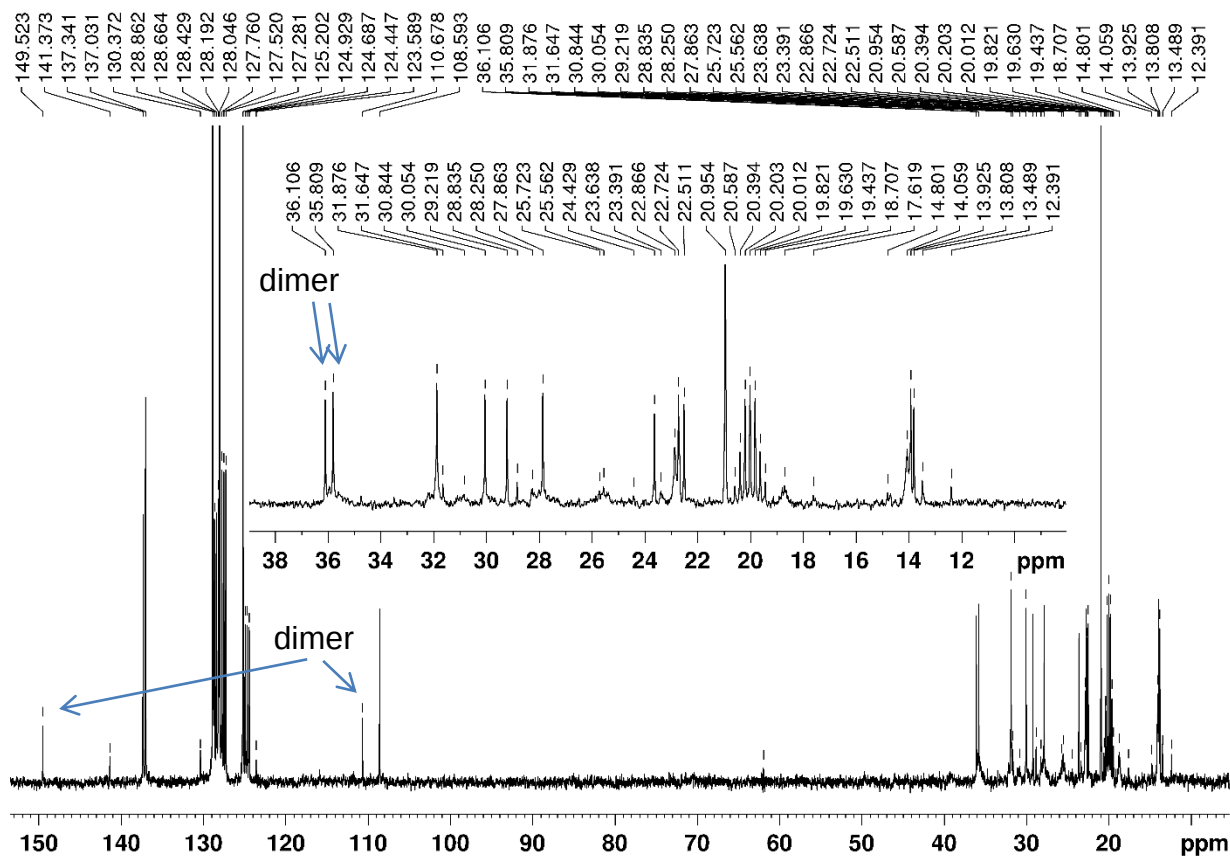


Figure S39. ^{13}C NMR of products obtained after the addition of hexene-1 to the system $\text{Me}_2\text{CInd}_2\text{ZrCl}_2$ (**1e**) – HAlBu^i_2 – MMAO-12 (1:4:8) in C_7D_8 , 333 K, 10 min.

