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

Lyudmila V. Parfenova [1,*], Pavel V. Kovyazin [1], Almira Kh. Bikmeeva [1], Eldar R. Palatov [1], Pavel V. Ivchenko [2,3], Ilya E. Nifant'ev [2,3]

[1] Institute of Petrochemistry and Catalysis, Ufa Federal Research Center, Russian Academy of Sciences, Prosp. Oktyabrya, 141, 450075 Ufa, Russia;
[2] Department of Chemistry, Lomonosov Moscow State University, 1-3 Leninskiye Gory, 119991 Moscow, Russia;
[3] A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky Prosp. 29, 119991 Moscow, Russia
***** Correspondence: luda_parfenova@ipc-ras.ru

Supporting Information

Figure S1. ^{1}H NMR of system Cp_2HfCl_2 (**1b**) − $HAlBu^{i}_2$ (1:3) in C_7D_8 (298 K).

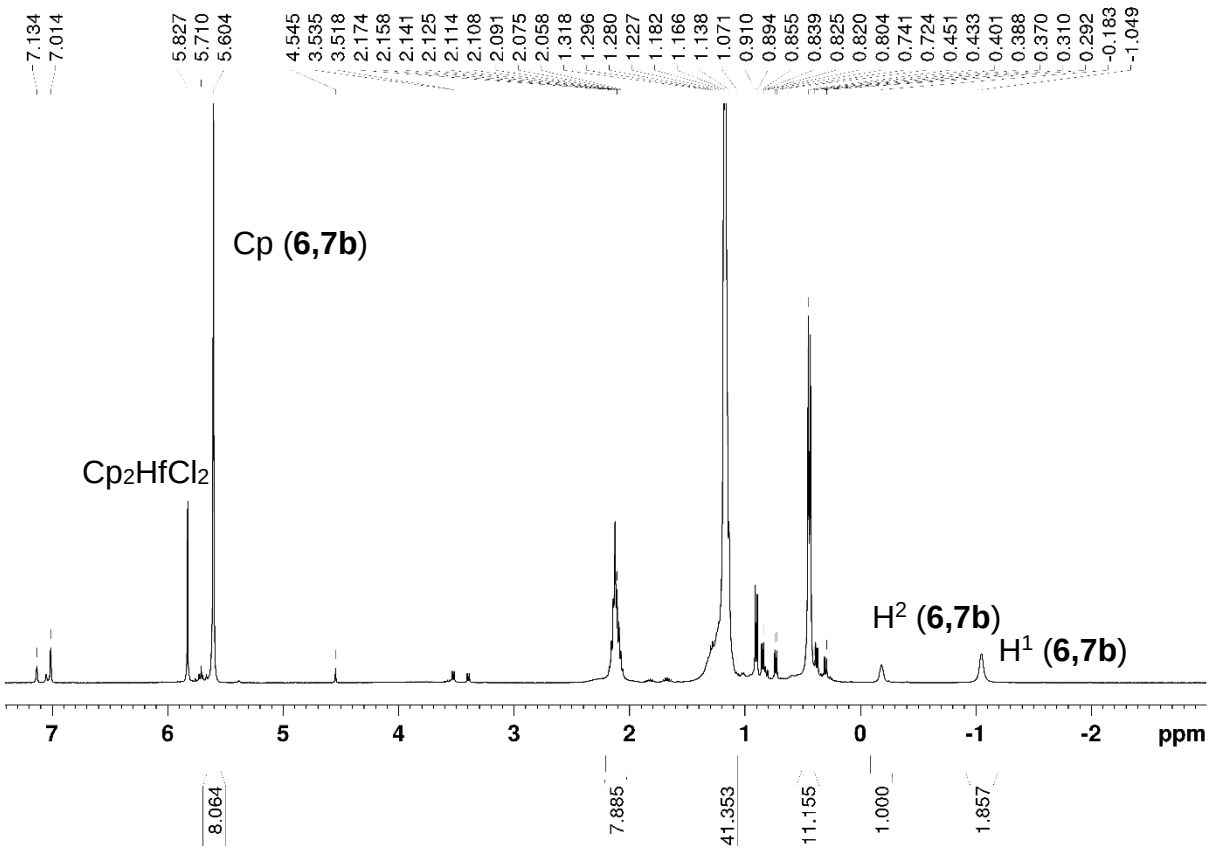

Figure S2. ^{13}C NMR of system Cp_2HfCl_2 (**1b**) − $HAlBu^{i}_2$ (1:3) in C_7D_8 (298 K).

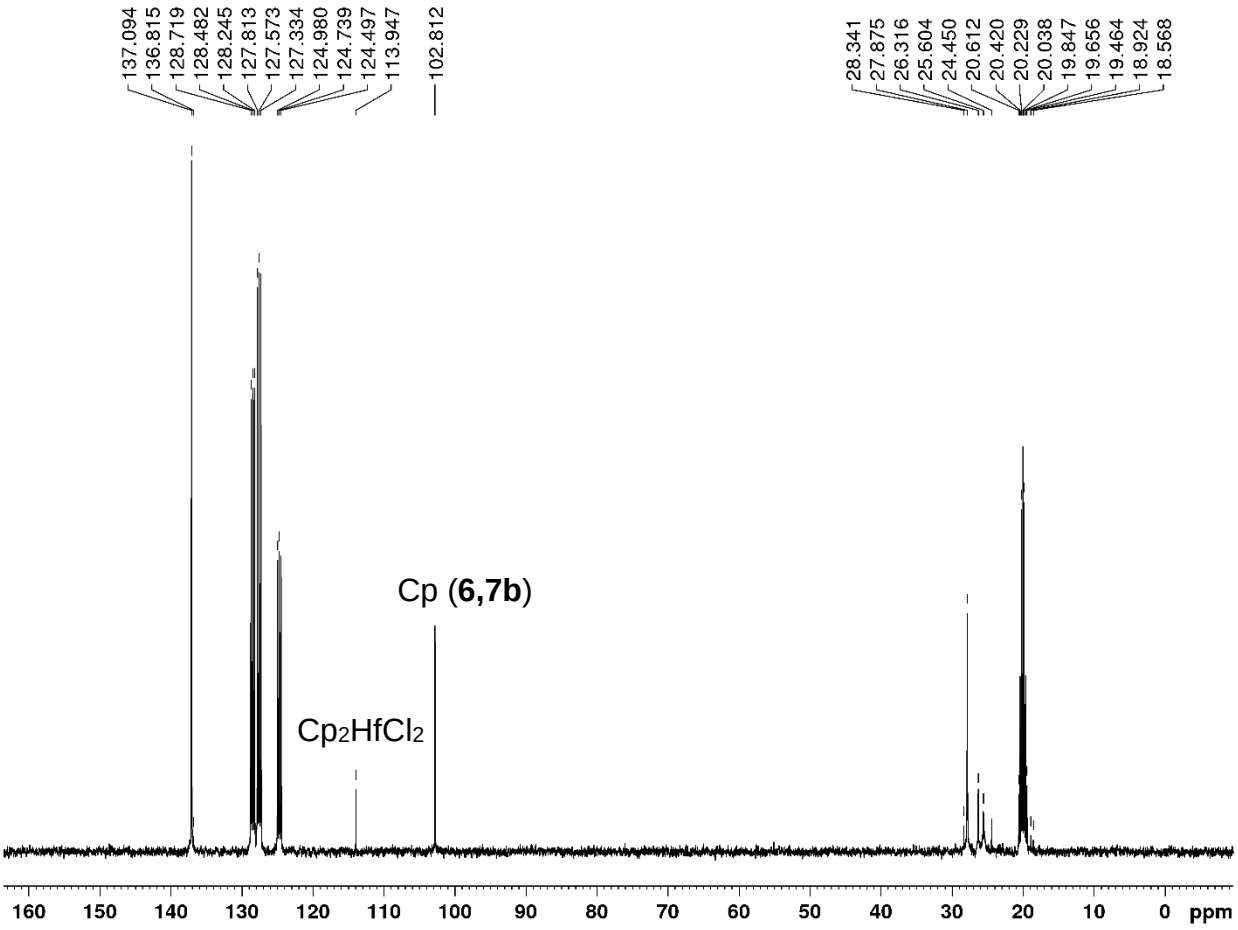

Figure S3. COSY HH of system Cp_2HfCl_2 (**1b**) − $HAlBu^i_2$ (1:3) in C_7D_8 (298 K).

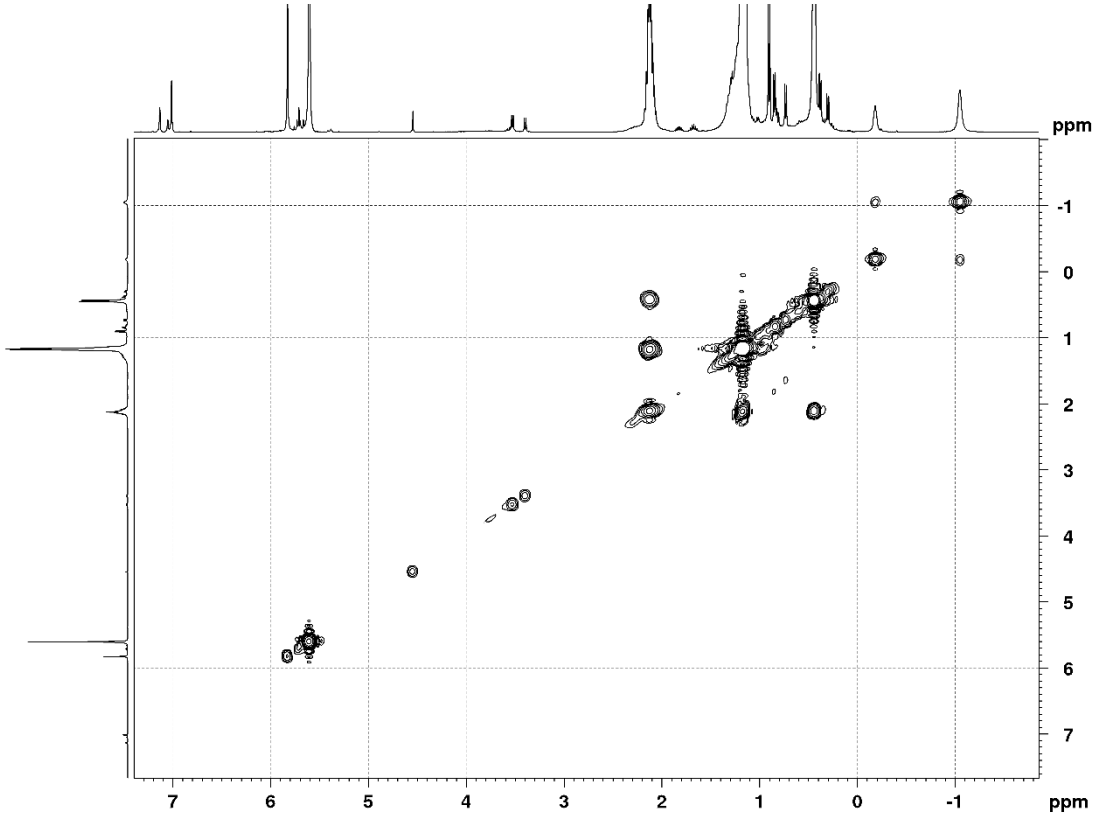

Figure S4. ^1H NMR of system Cp_2HfCl_2 (**1b**) − $HAlBu^i_2$ (1:14) in C_7D_8 (298 K).

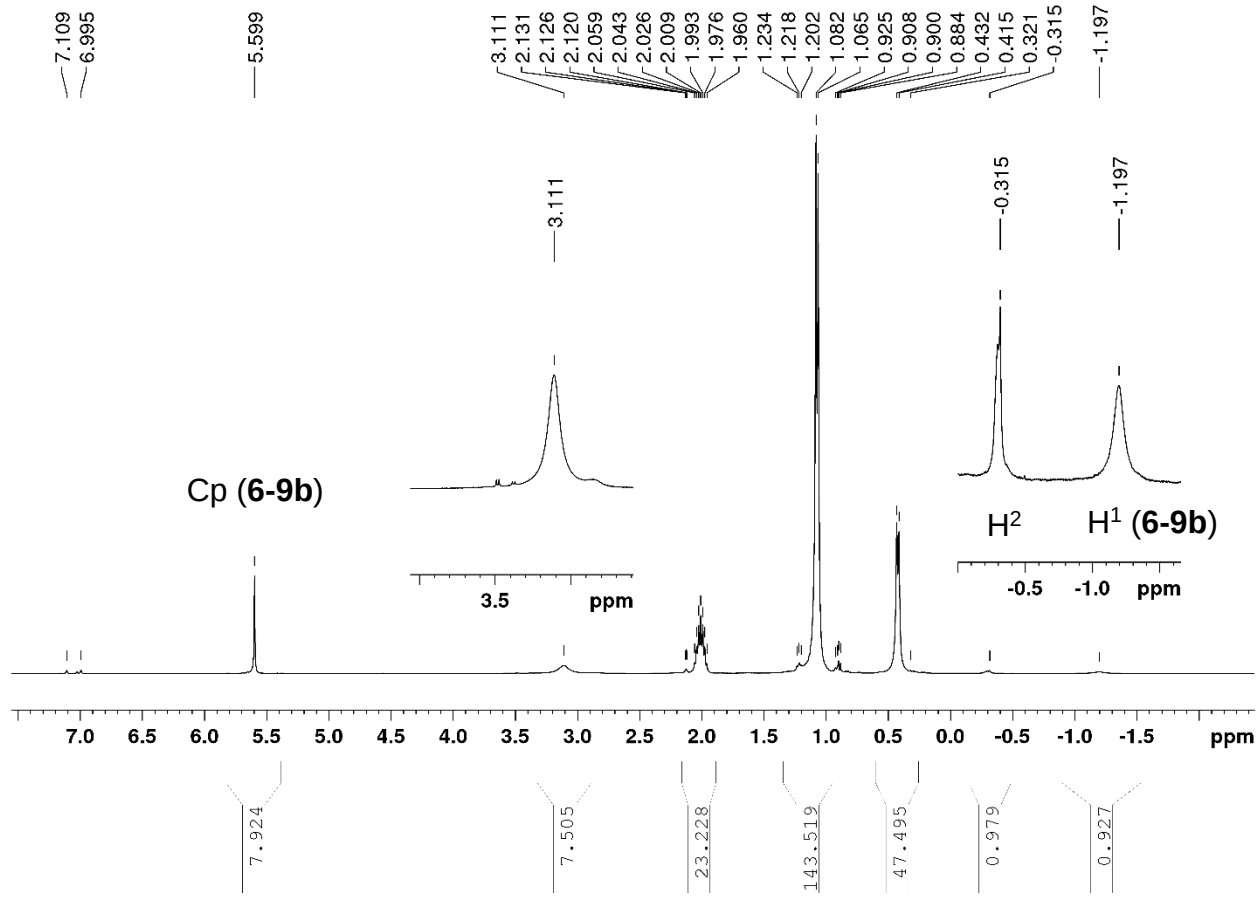

Figure S5. NOESY of system Cp_2HfCl_2 (**1b**) − $HAlBu^i_2$ (1:14) in C_7D_8 (298 K).

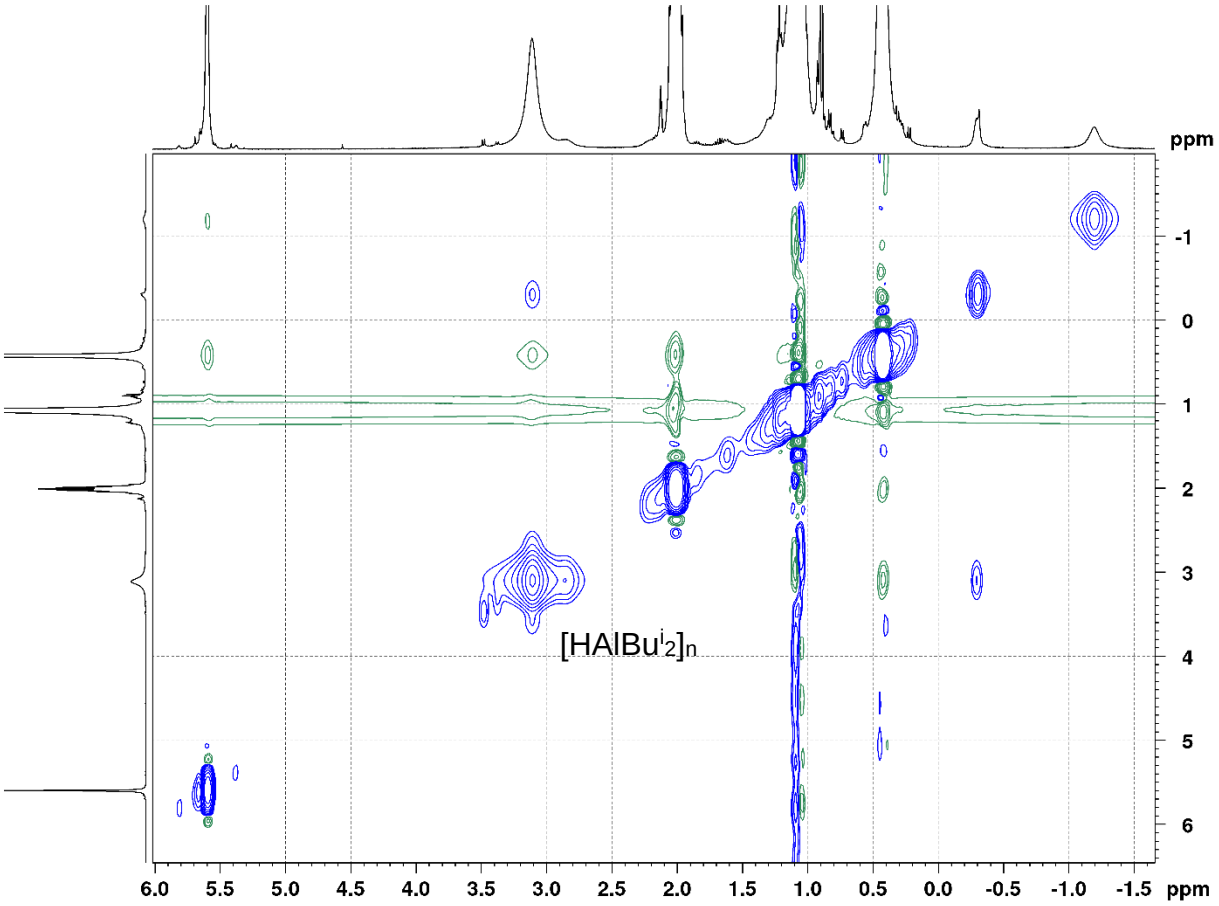

Figure S6. ^1H NMR of system Cp_2HfCl_2 (**1b**) − $HAlBu^i_2$ − MMAO-12 (1:14:9) in C_7D_8 (298 K).

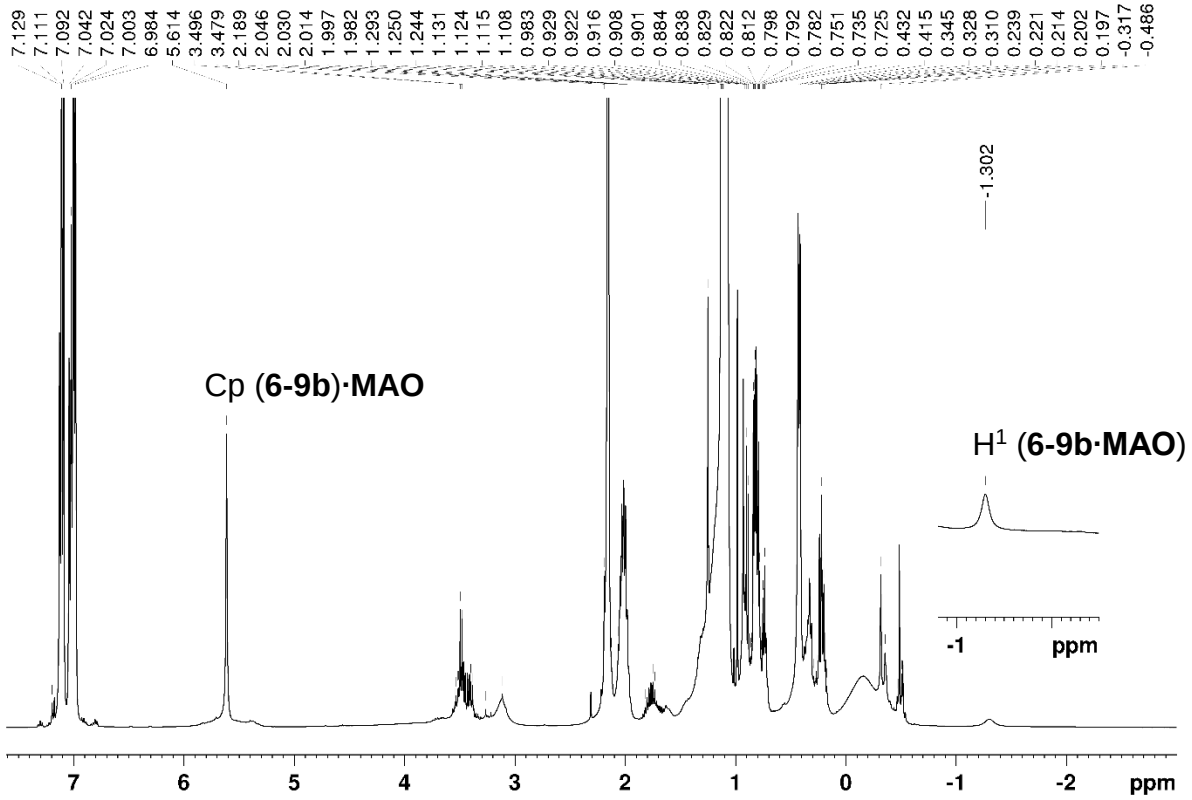

Figure S7. ^{1}H NMR of system Cp_2HfCl_2 (**1b**) − $HAlBu^i_2$ − MMAO-12 (1:4:13) in C_7D_8 (298 K).

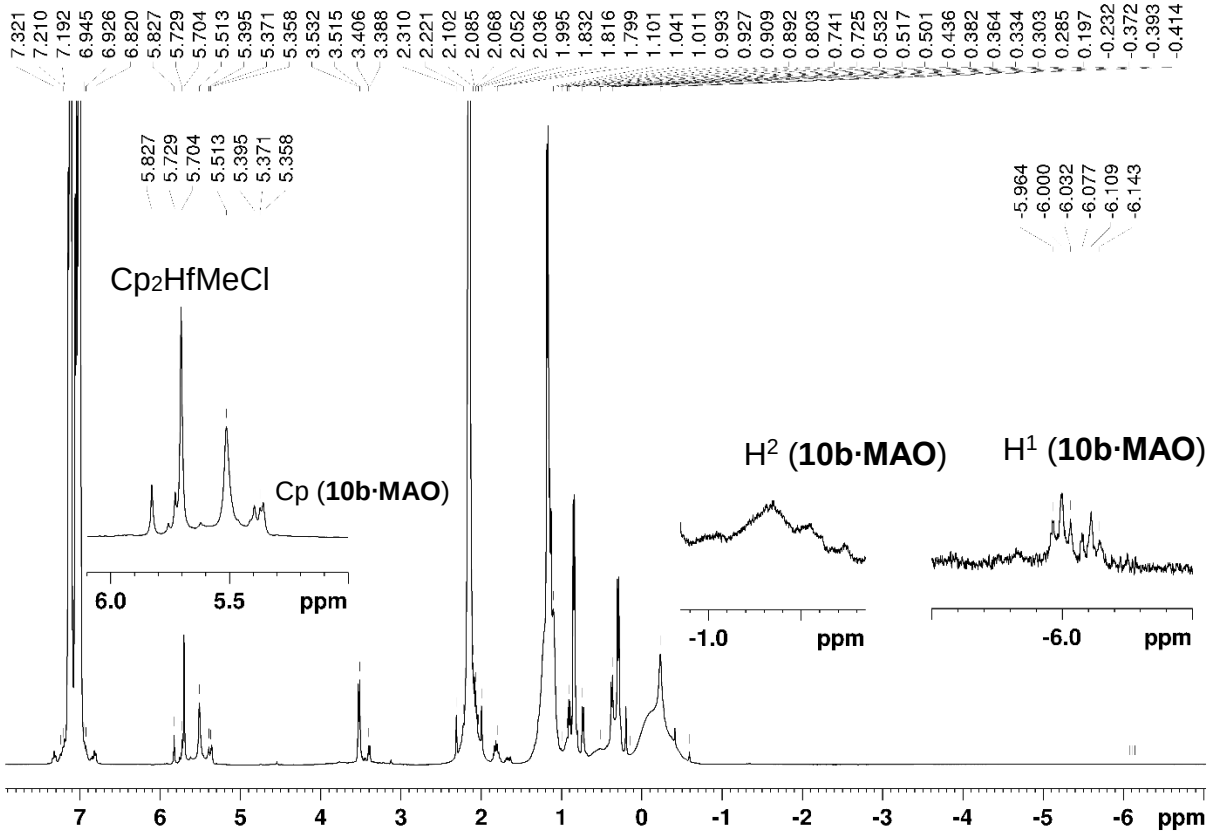

Figure S8. COSY HH of system Cp_2HfCl_2 (**1b**) − $HAlBu^i_2$ − MMAO-12 (1:4:13) in C_7D_8 (298 K).

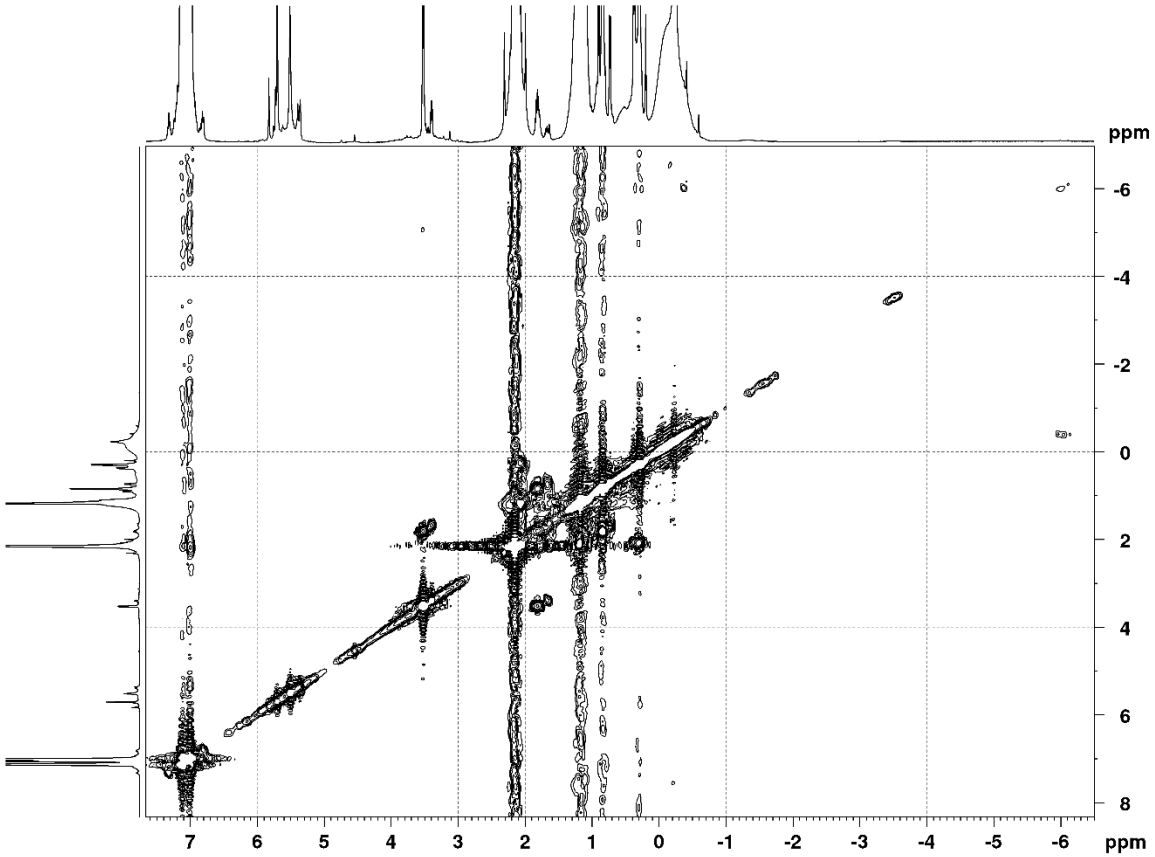

Figure S9. NOESY of system Cp_2HfCl_2 (**1b**) − $HAlBu^i_2$ − MMAO-12 (1:14:9) in C_7D_8 (298 K).

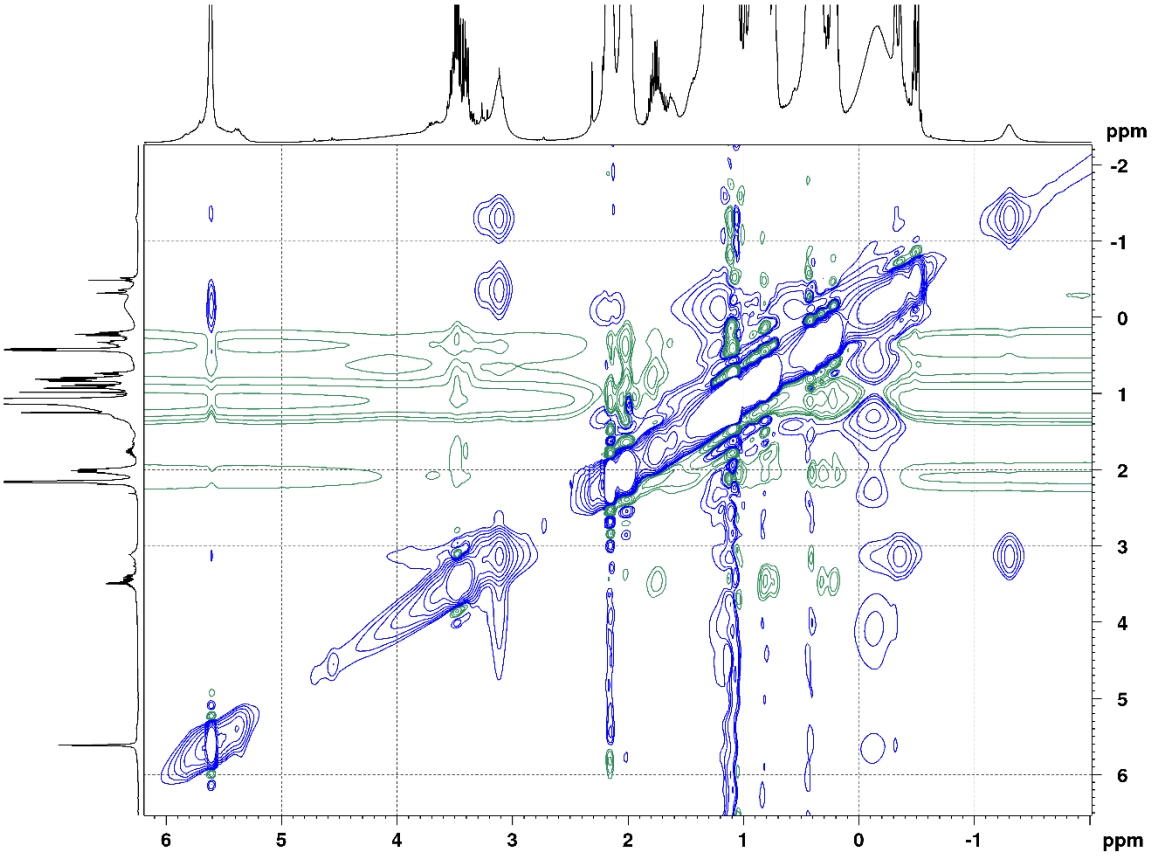

Figure S10. ^1H NMR of system $(CpMe)_2ZrCl_2$ (**1c**) − $HAlBu^i_2$ (1:4) in C_7D_8 (298 K).

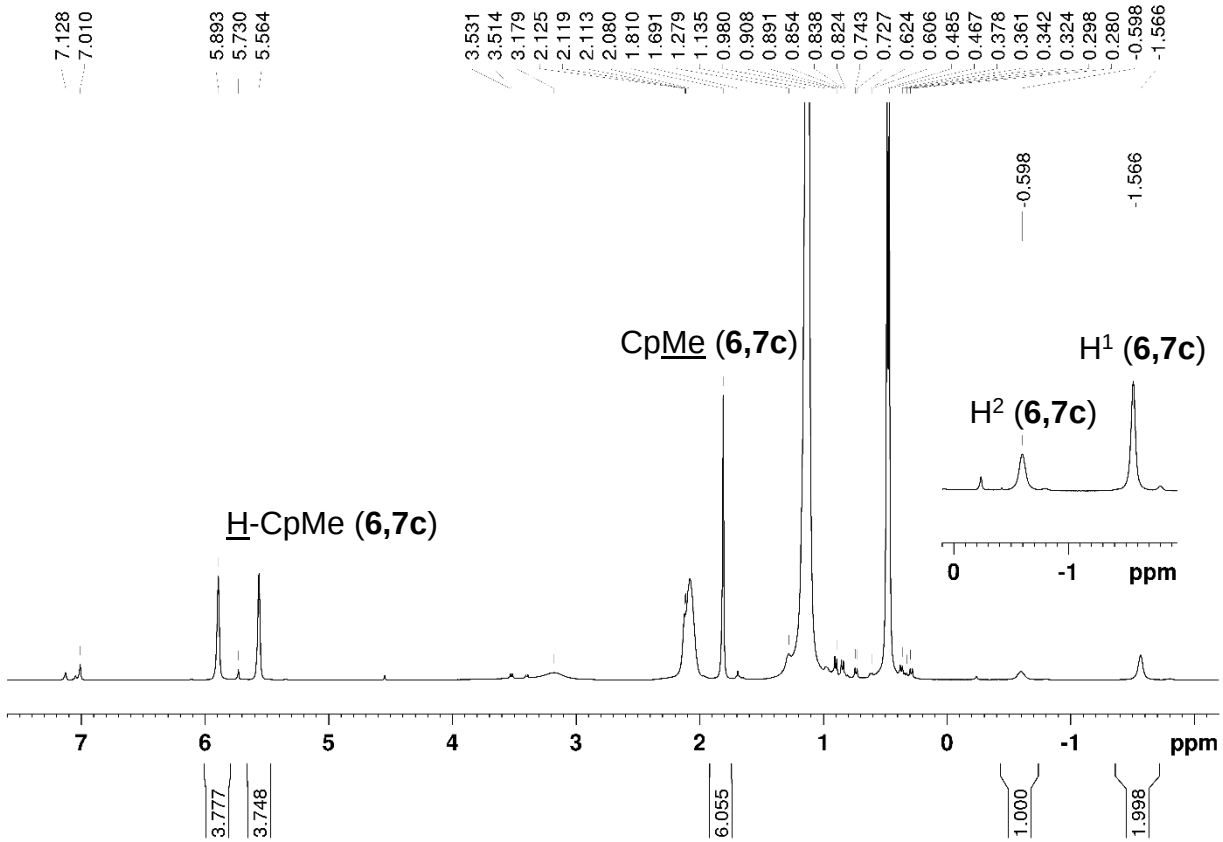

Figure S11. ^{13}C NMR of system $(CpMe)_2ZrCl_2$ (**1c**) − $HAlBu^i_2$ (1:4) in C_7D_8 (298 K).

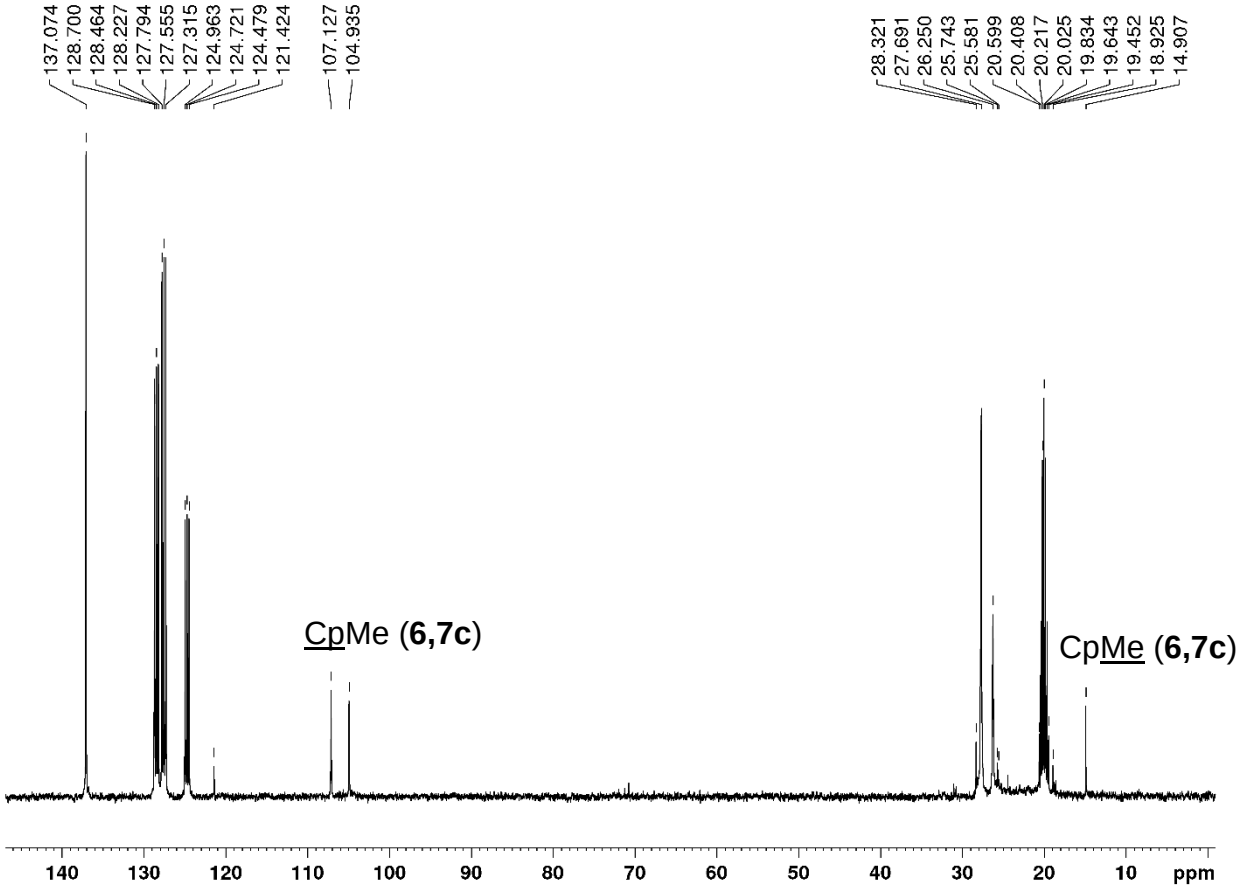

Figure S12. NOESY of system $(CpMe)_2ZrCl_2$ (**1c**) − $HAlBu^i_2$ (1:4) in C_7D_8 (298 K).

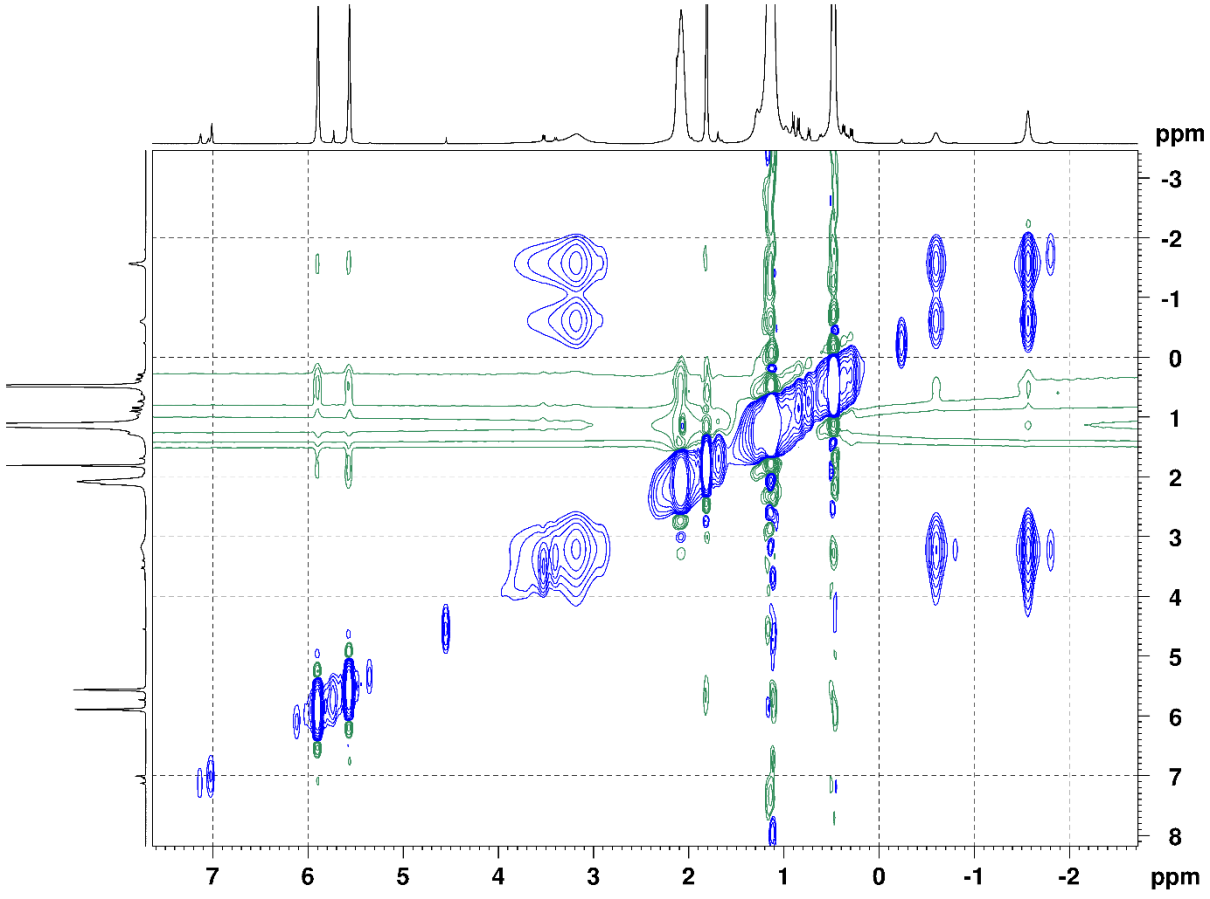

Figure S13. ^{1}H NMR of system $(CpMe)_2ZrCl_2$ (**1c**) − $HAlBu^{i}_2$ (1:7) in C_7D_8 (298 K).

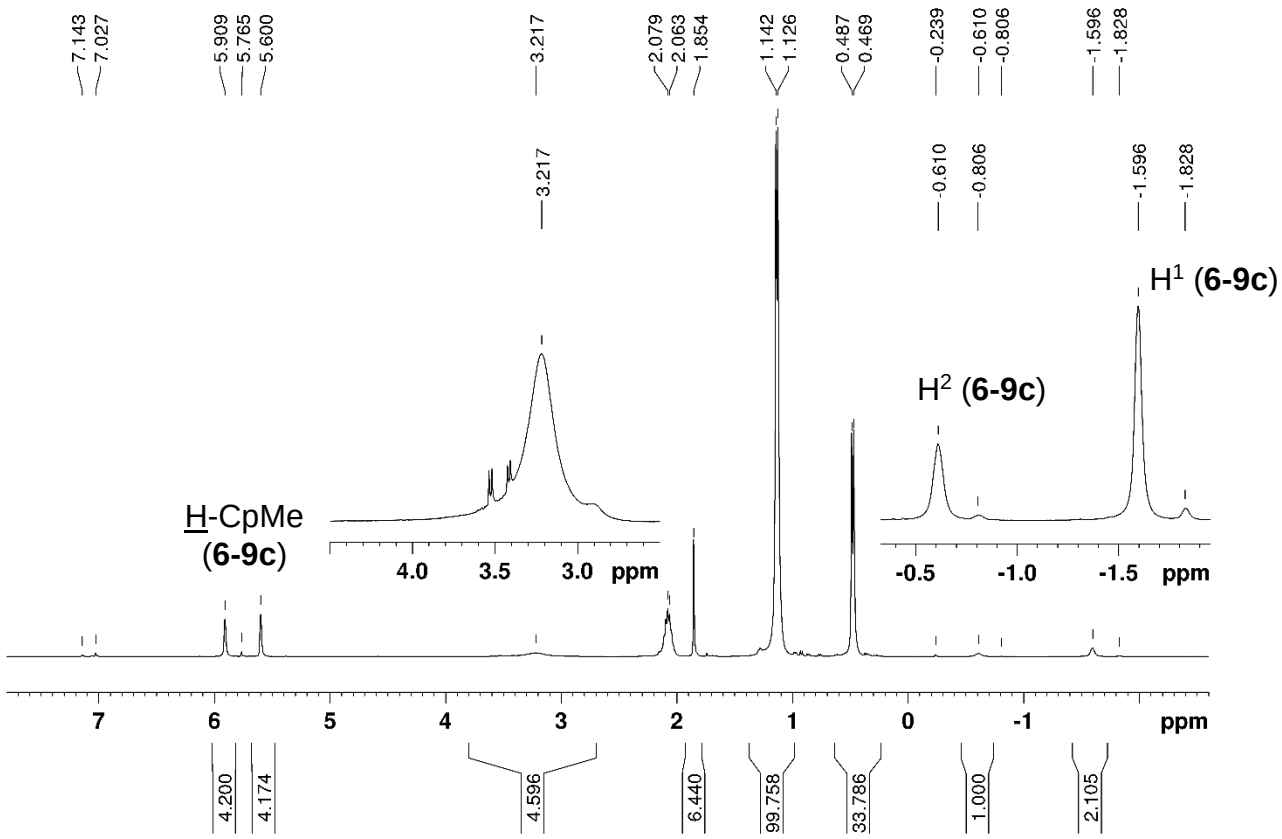

Figure S14. ^{1}H NMR of system $(CpMe)_2ZrCl_2$ (**1c**) − $HAlBu^{i}_2$ – MMAO-12 (1:7:6) in C_7D_8 (298 K).

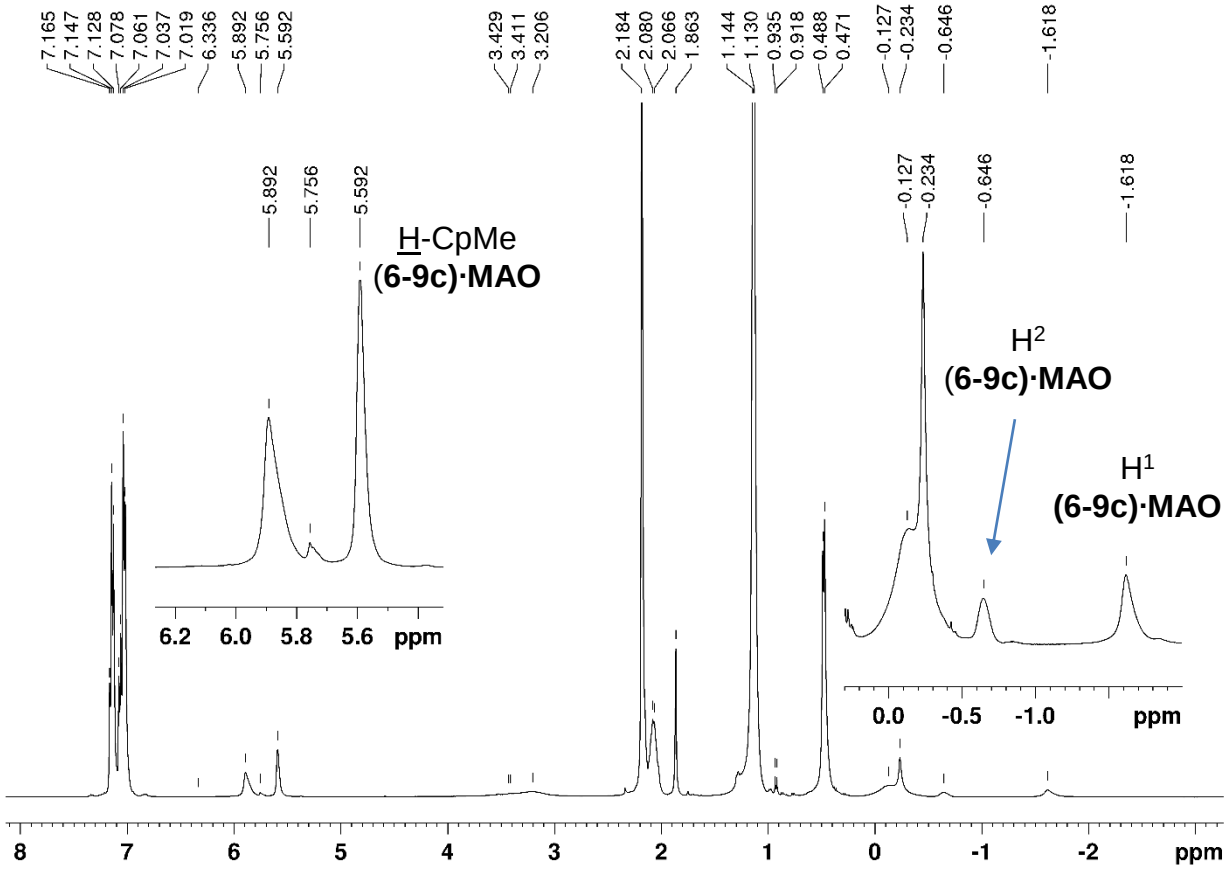

Figure S15. NOESY of system $(CpMe)_2ZrCl_2$ (**1c**) − $HAlBu^i_2$ – MMAO-12 (1:7:6) in C_7D_8 (298 K).

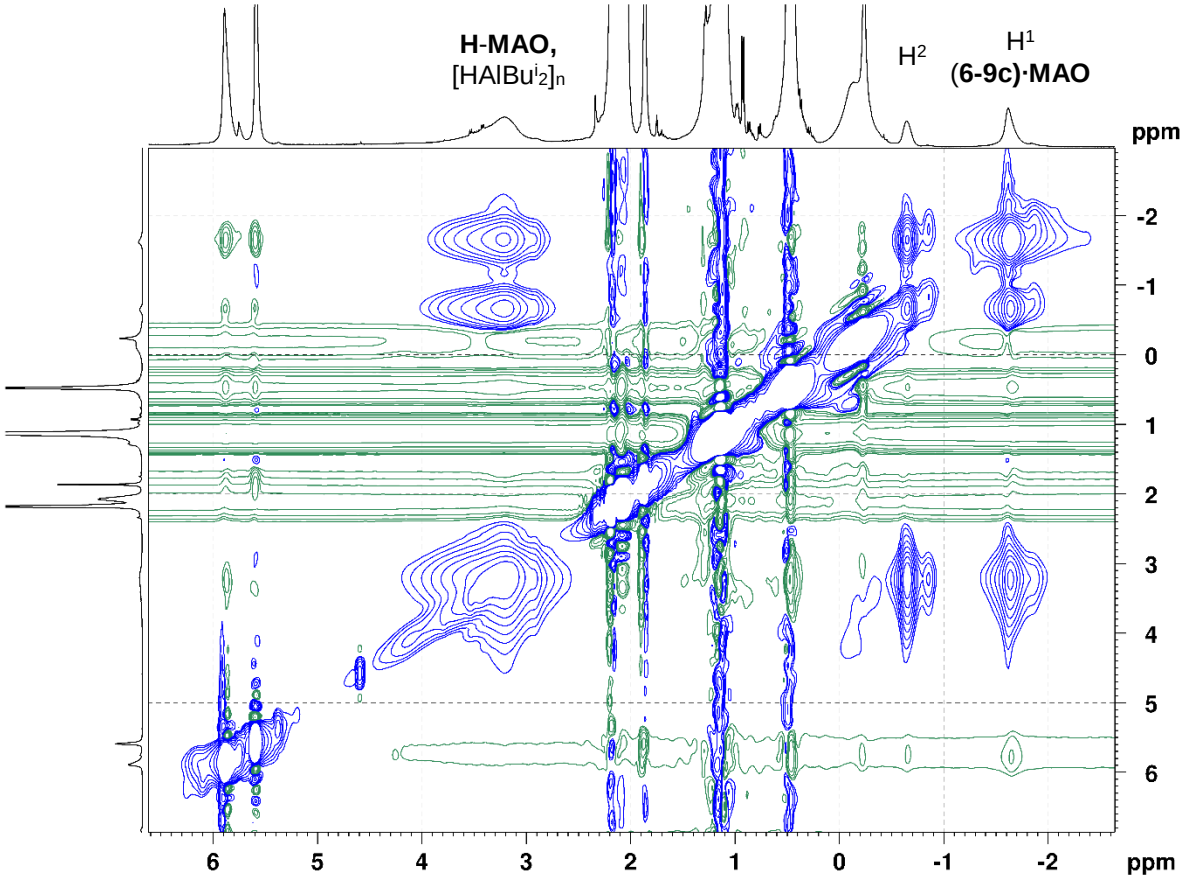

Figure S16. ^1H NMR of system $(CpMe)_2ZrCl_2$ (**1c**) − $HAlBu^i_2$ – MMAO-12 (1:4:11) in C_7D_8 (298 K), reaction time – 6 h.

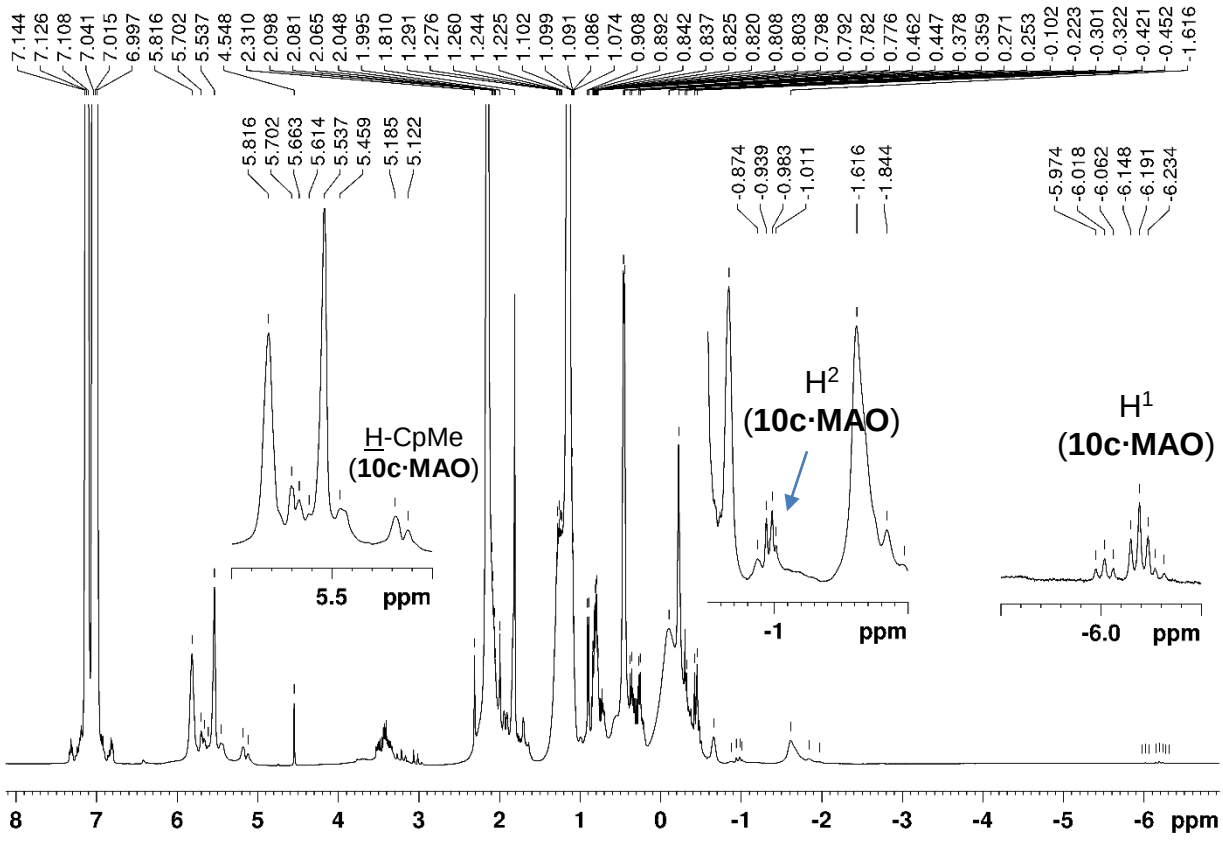

Figure S17. COSY HH of system $(CpMe)_2ZrCl_2$ (**1c**) − $HAlBu^i_2$ – MMAO-12 (1:4:11) in C_7D_8 (298 K), reaction time – 6 h.

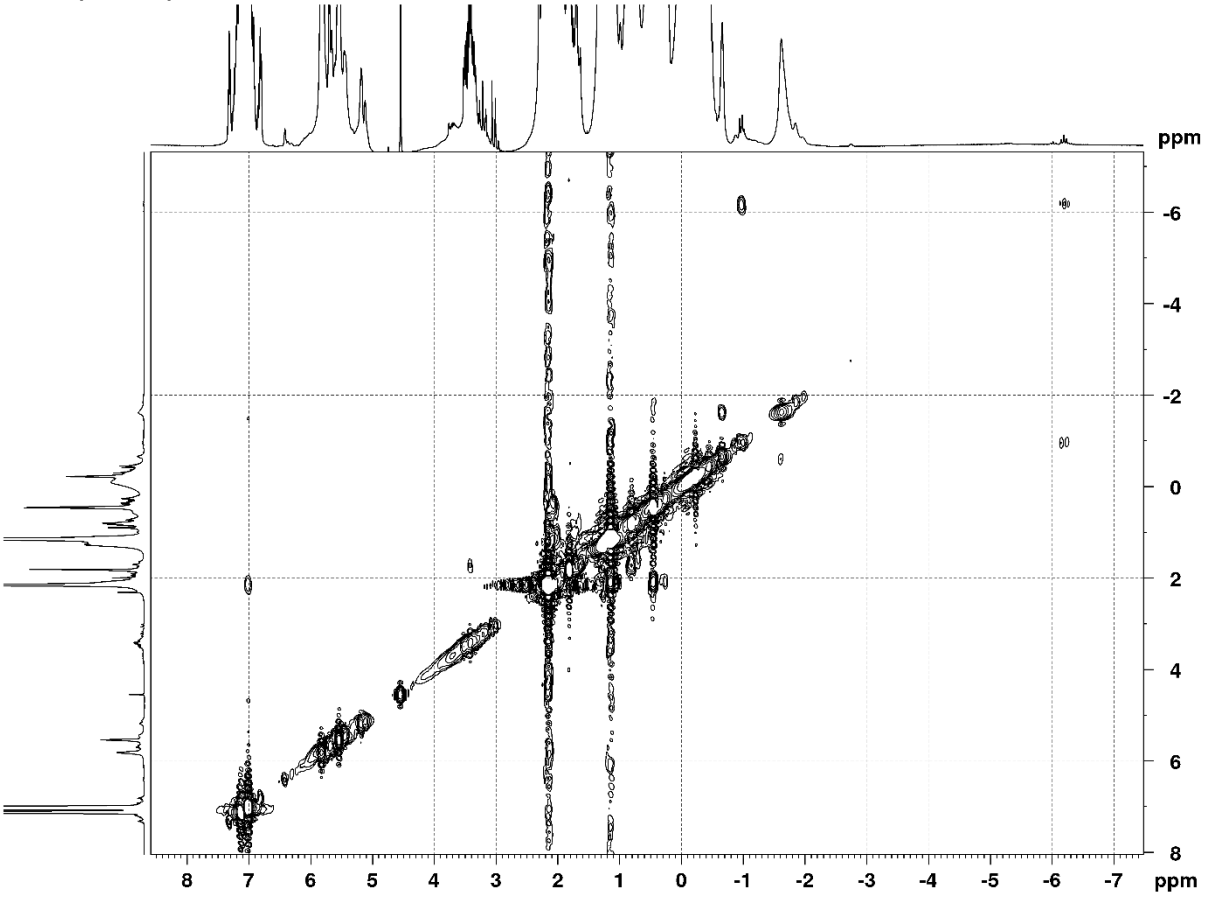

Figure S18. ^1H NMR of system *ansa*-$Me_4C_2Cp_2ZrCl_2$ (**1d**) − $HAlBu^i_2$ (1:5) in C_7D_8 (298 K).

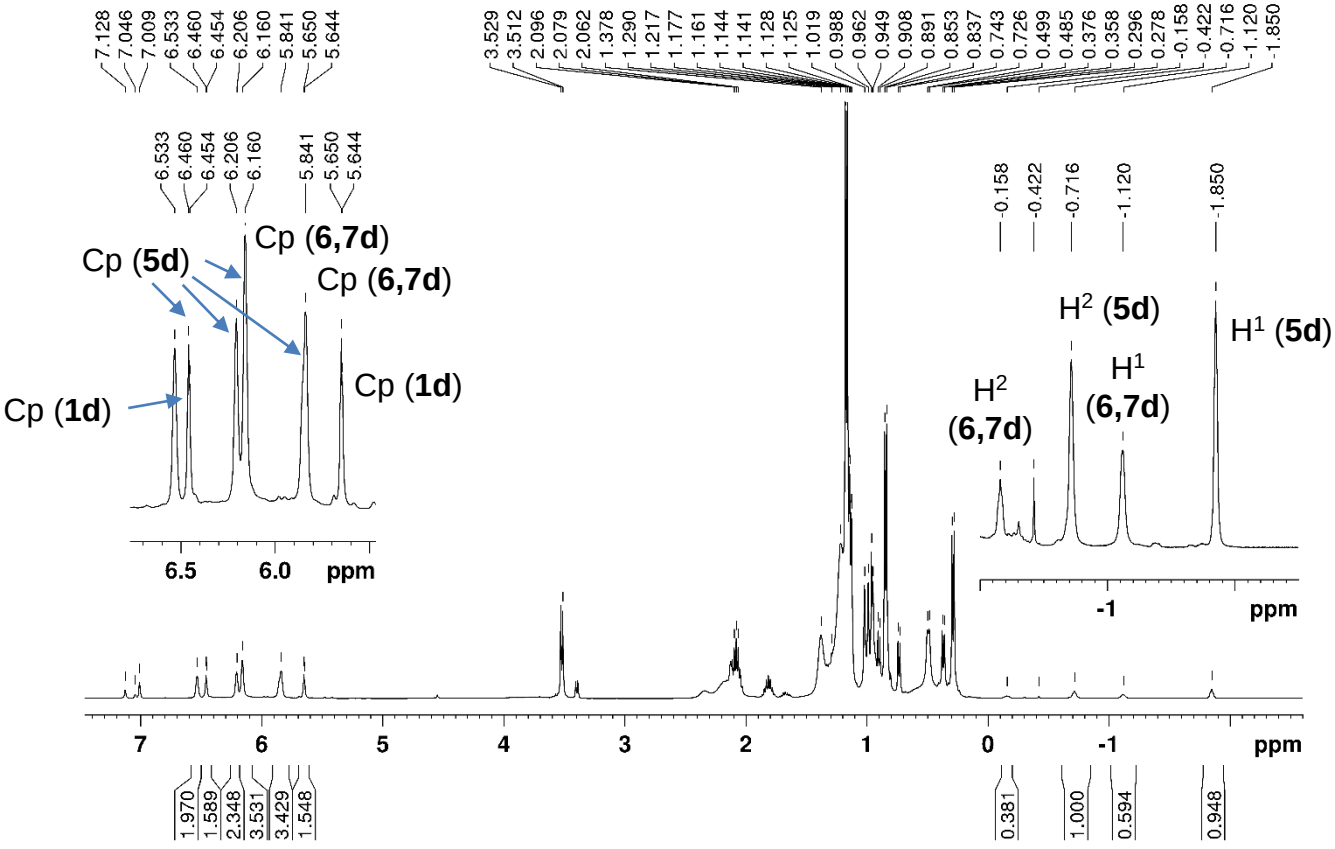

Figure S19. ^{13}C NMR of system *ansa*-$Me_4C_2Cp_2ZrCl_2$ (**1d**) − $HAlBu^i_2$ (1:5) in C_7D_8 (298 K).

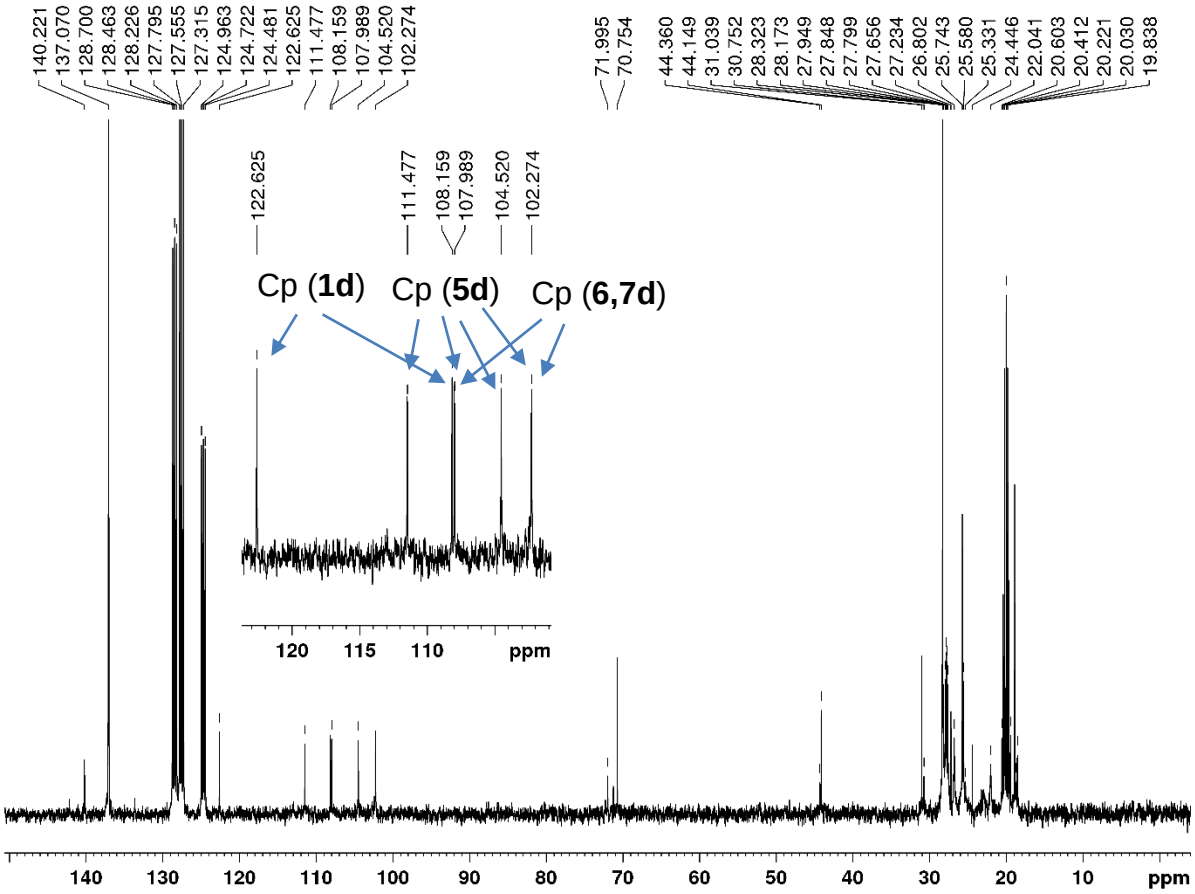

Figure S20. COSY HH of system *ansa*-$Me_4C_2Cp_2ZrCl_2$ (**1d**) − $HAlBu^i_2$ (1:5) in C_7D_8 (298 K).

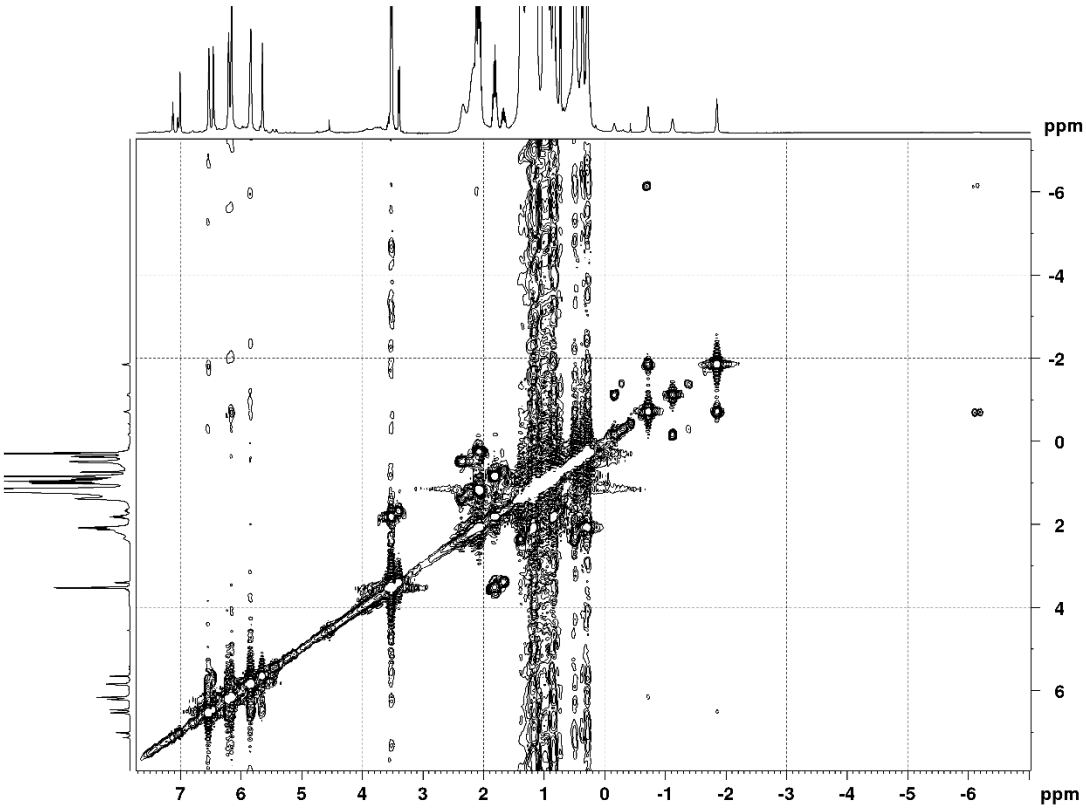

Figure S21. NOESY of system *ansa*-$Me_4C_2Cp_2ZrCl_2$ (**1d**) − $HAlBu^i_2$ (1:5) in C_7D_8 (298 K).

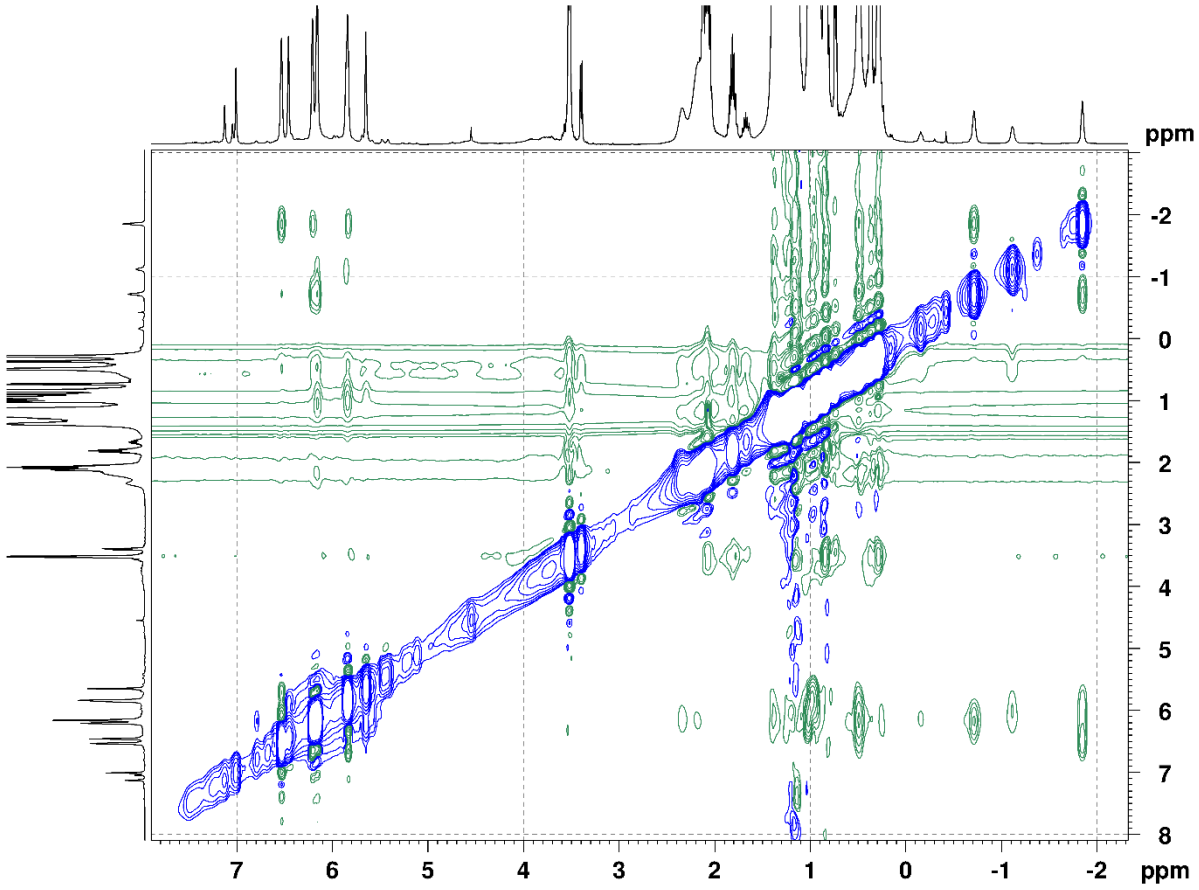

Figure S22. ^1H NMR of system *ansa*-$Me_4C_2Cp_2ZrCl_2$ (**1d**) − $HAlBu^i_2$ (1:8) in C_7D_8 (298 K).

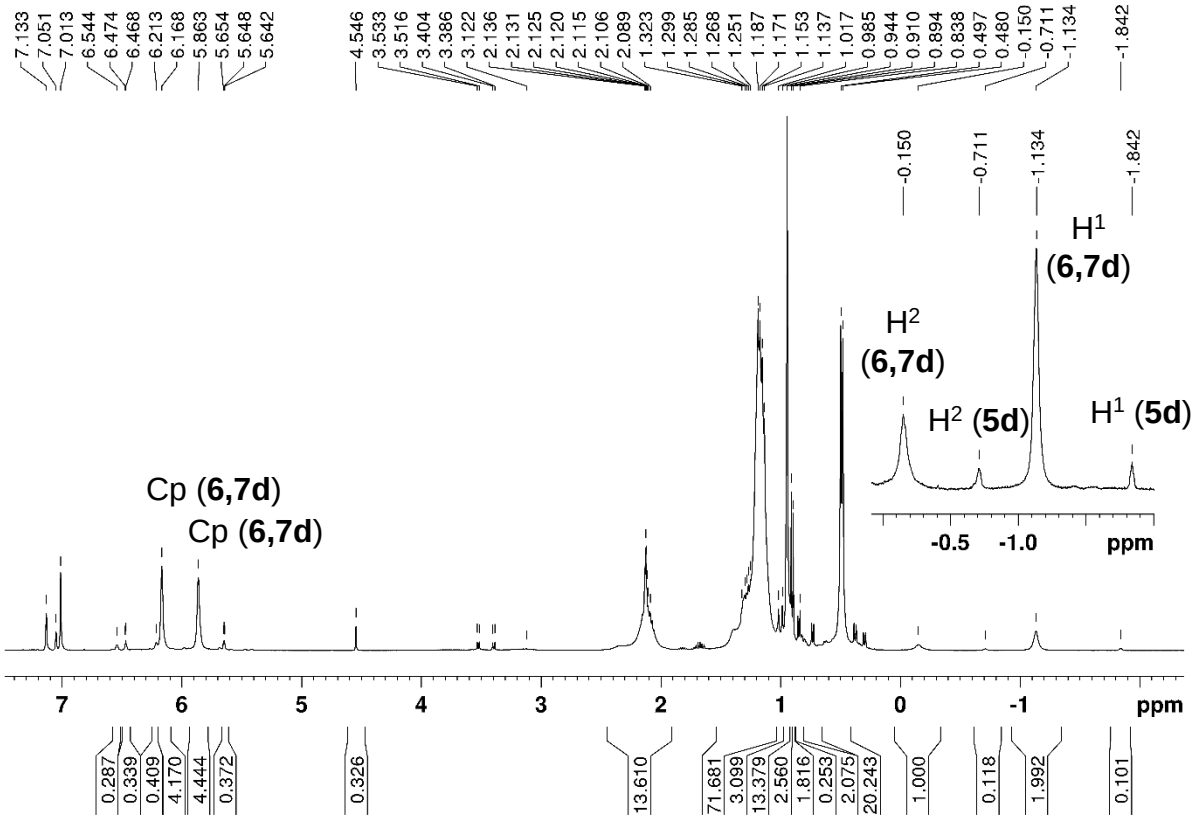

Figure S23. ^{1}H NMR of system *ansa*-$Me_4C_2Cp_2ZrCl_2$ (**1d**) − $HAlBu^i_2$ (1:14) in C_7D_8 (298 K).

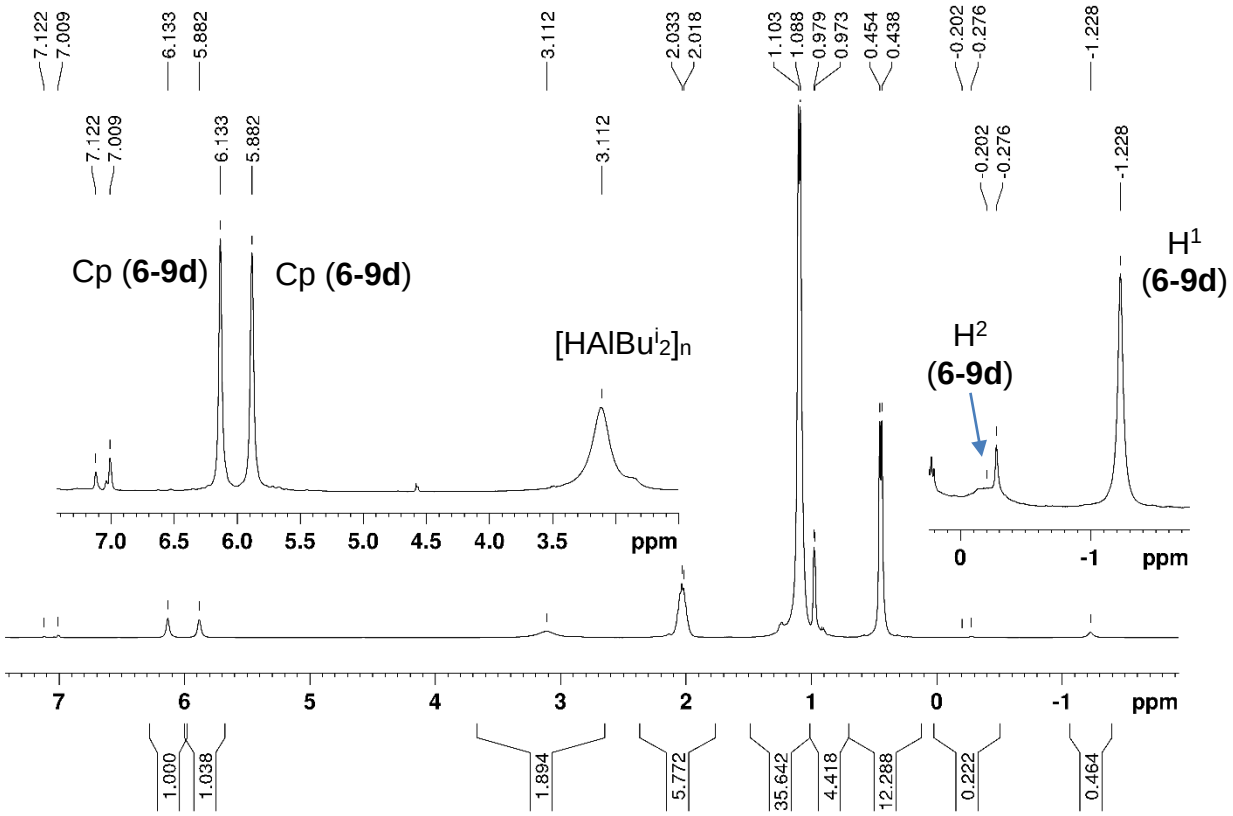

Figure S24. NOESY of system *ansa*-$Me_4C_2Cp_2ZrCl_2$ (**1d**) − $HAlBu^i_2$ (1:14) in C_7D_8 (298 K).

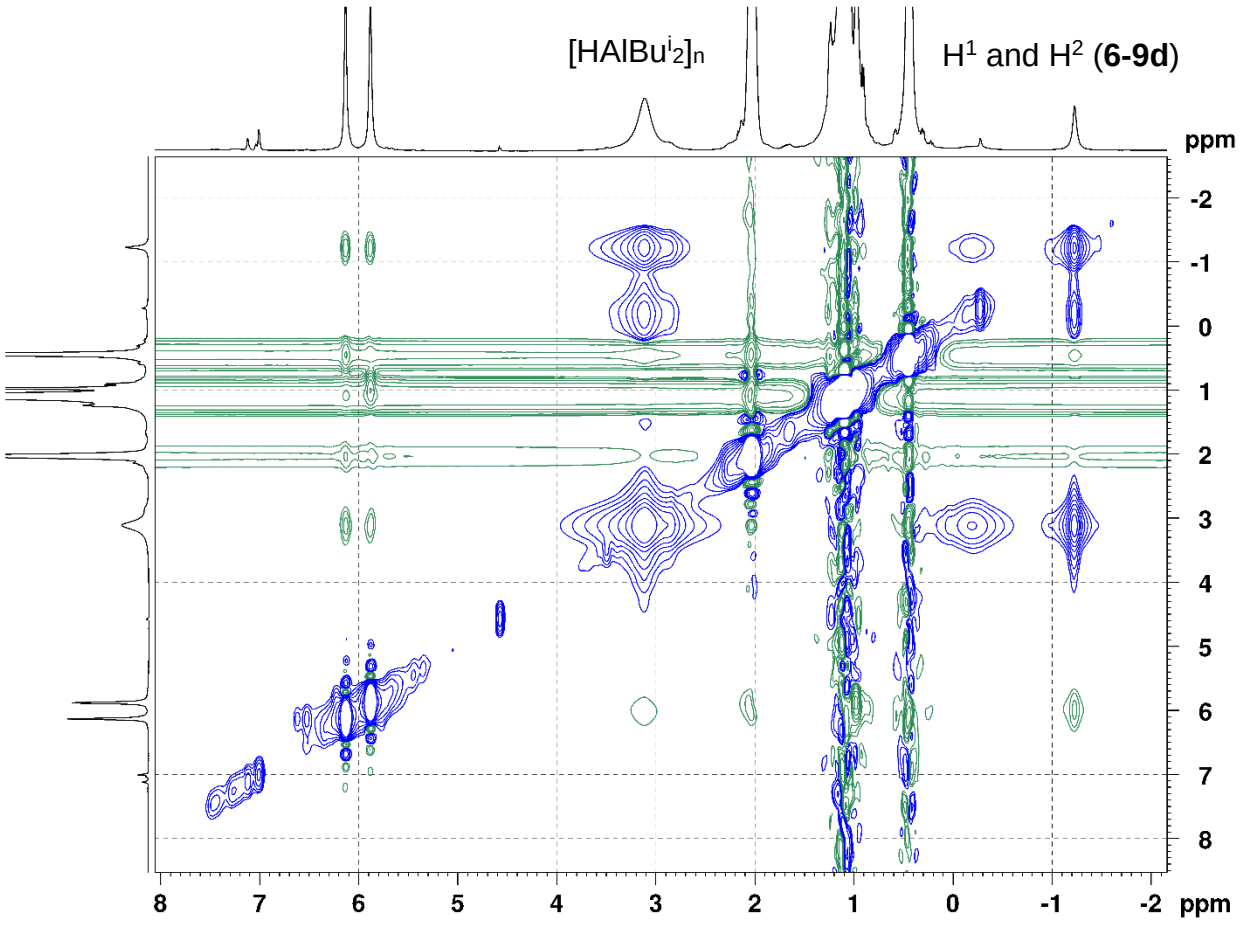

Figure S25. ^{1}H NMR of system *ansa*-$Me_4C_2Cp_2ZrCl_2$ (**1d**) − $HAlBu^{i}_2$ – MMAO-12 (1:5:14) in C_7D_8 (298 K).

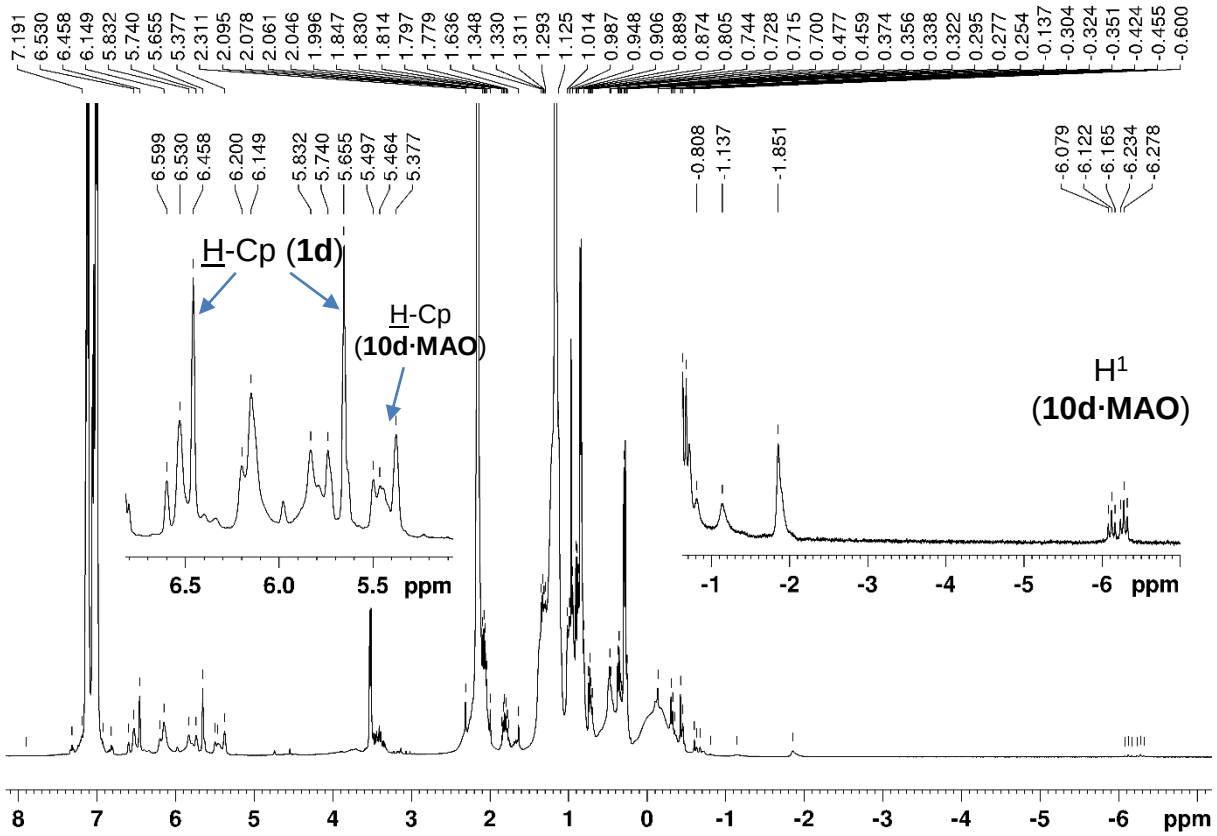

Figure S26. COSY HH of system *ansa*-$Me_4C_2Cp_2ZrCl_2$ (**1d**) − $HAlBu^{i}_2$ – MMAO-12 (1:5:14) in C_7D_8 (298 K).

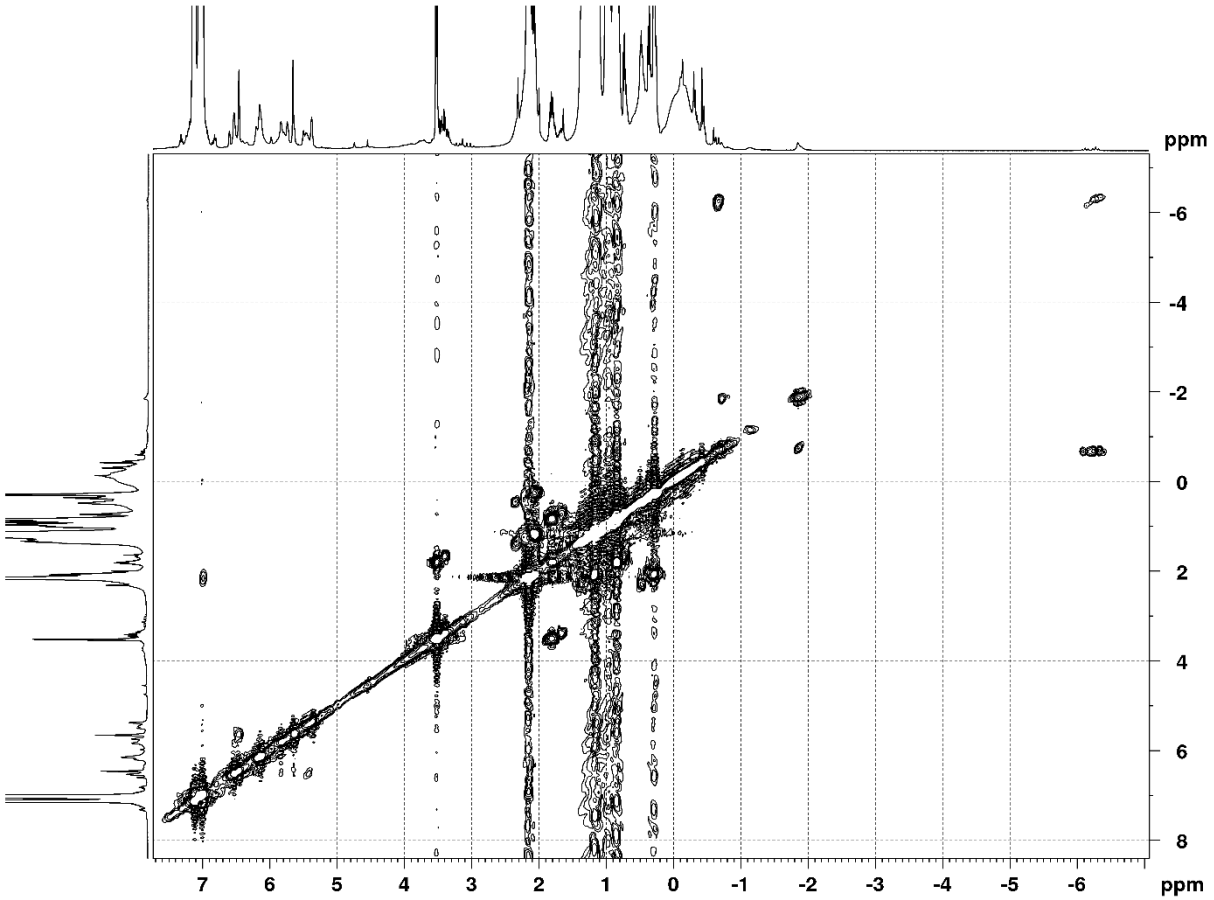

Figure S27. NOESY of system *ansa*-$Me_4C_2Cp_2ZrCl_2$ (**1d**) − $HAlBu^i_2$ – MMAO-12 (1:5:14) in C_7D_8 (298 K).

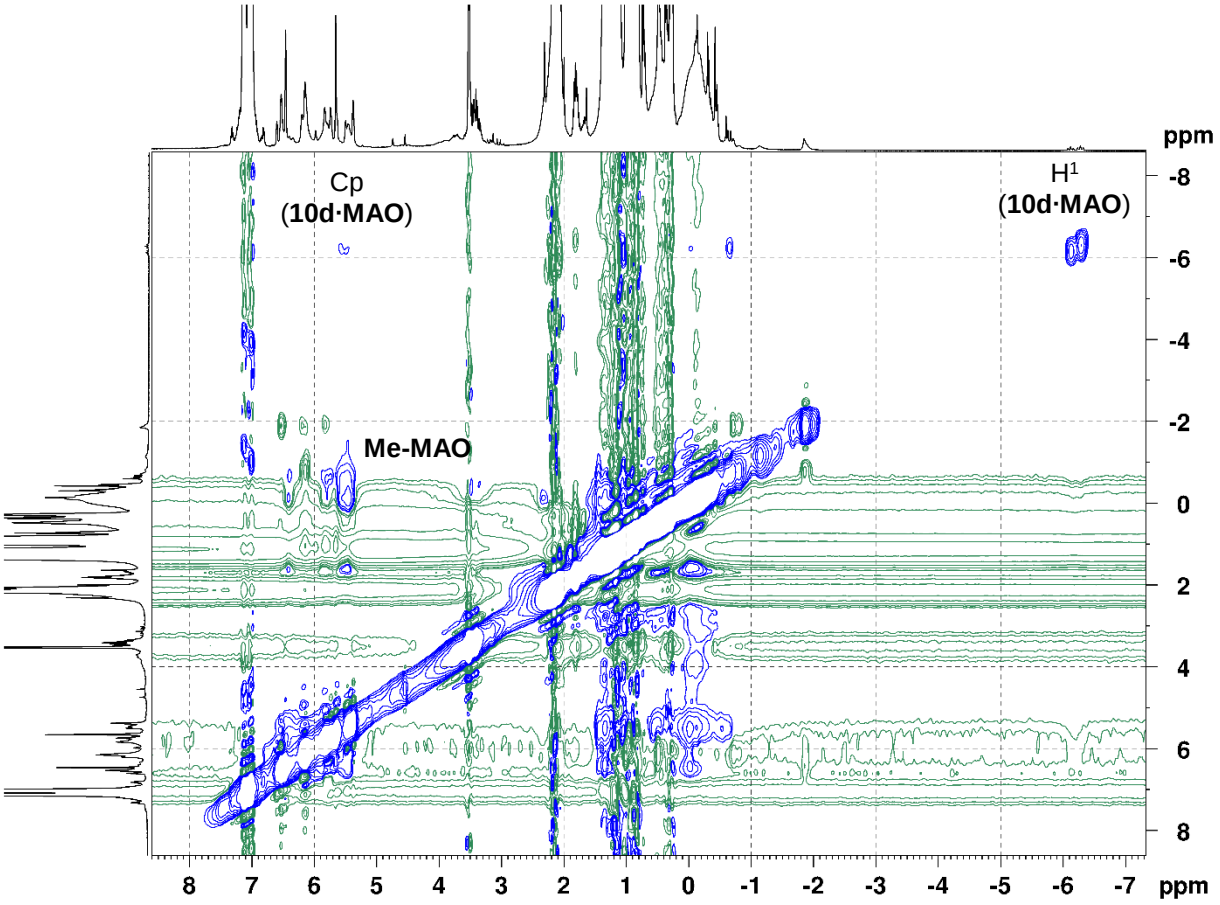

Figure S28. ^1H NMR of system *ansa*-$Me_4C_2Cp_2ZrCl_2$ (**1d**) − $HAlBu^i_2$ (1:2) in $CDCl_3$ (298 K).

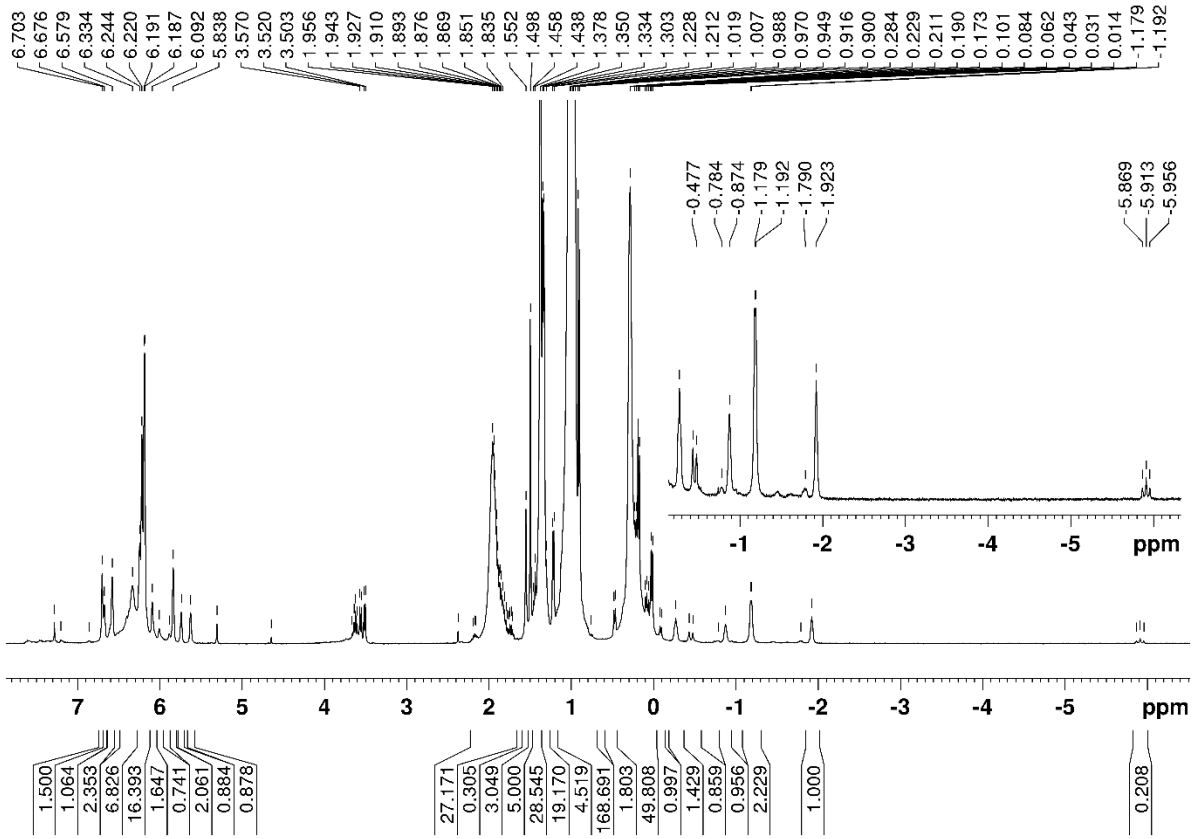

Figure S29. ^{1}H NMR of system *ansa*-$Me_4C_2Cp_2ZrCl_2$ (**1d**) − $HAlBu^i_2$ – MMAO-12 (1:2:3) in $CDCl_3$ (298 K).

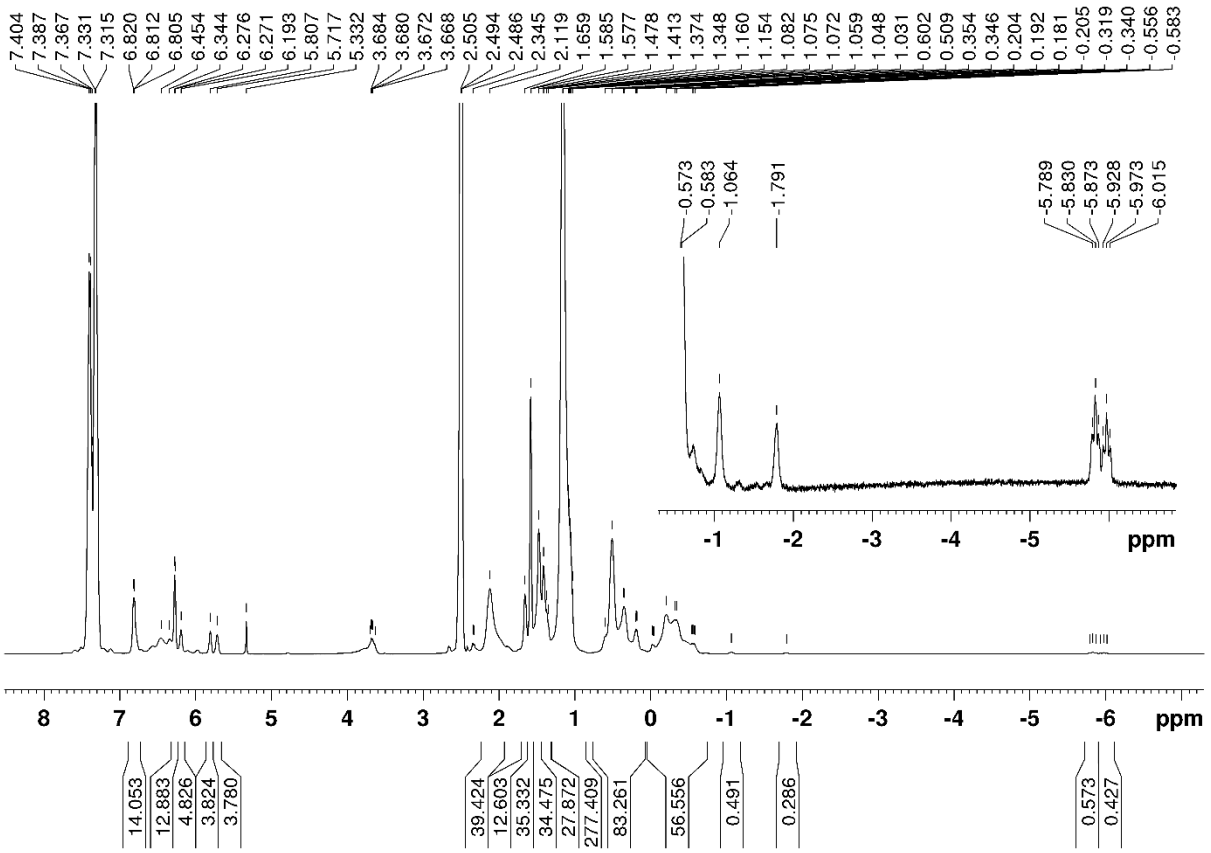

Figure S30. ^{1}H NMR of system *ansa*-$Me_4C_2Cp_2ZrCl_2$ (**1d**) − $HAlBu^i_2$ – MMAO-12 (1:14:8) in C_7D_8 (298 K).

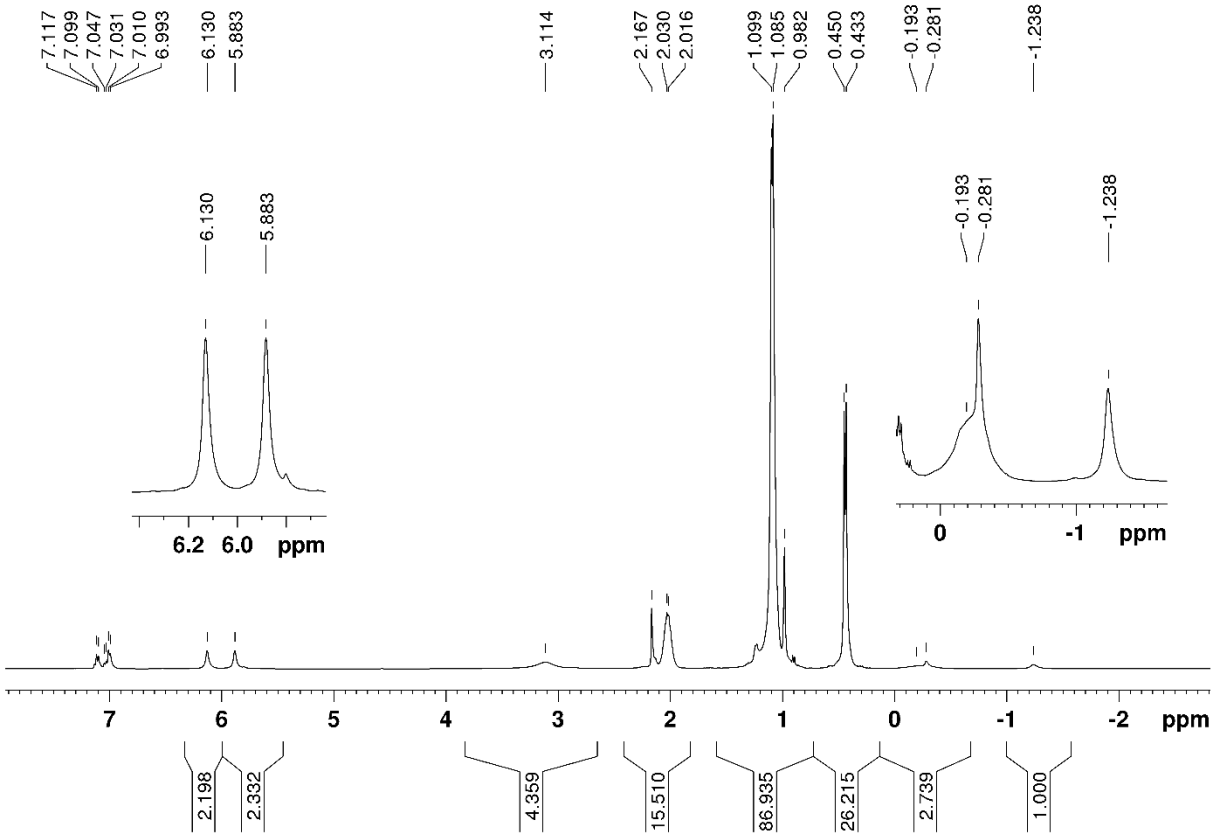

Figure S31. NOESY of system *ansa*-$Me_4C_2Cp_2ZrCl_2$ (**1d**) − $HAlBu^i_2$ – MMAO-12 (1:14:8) in C_7D_8 (298 K).

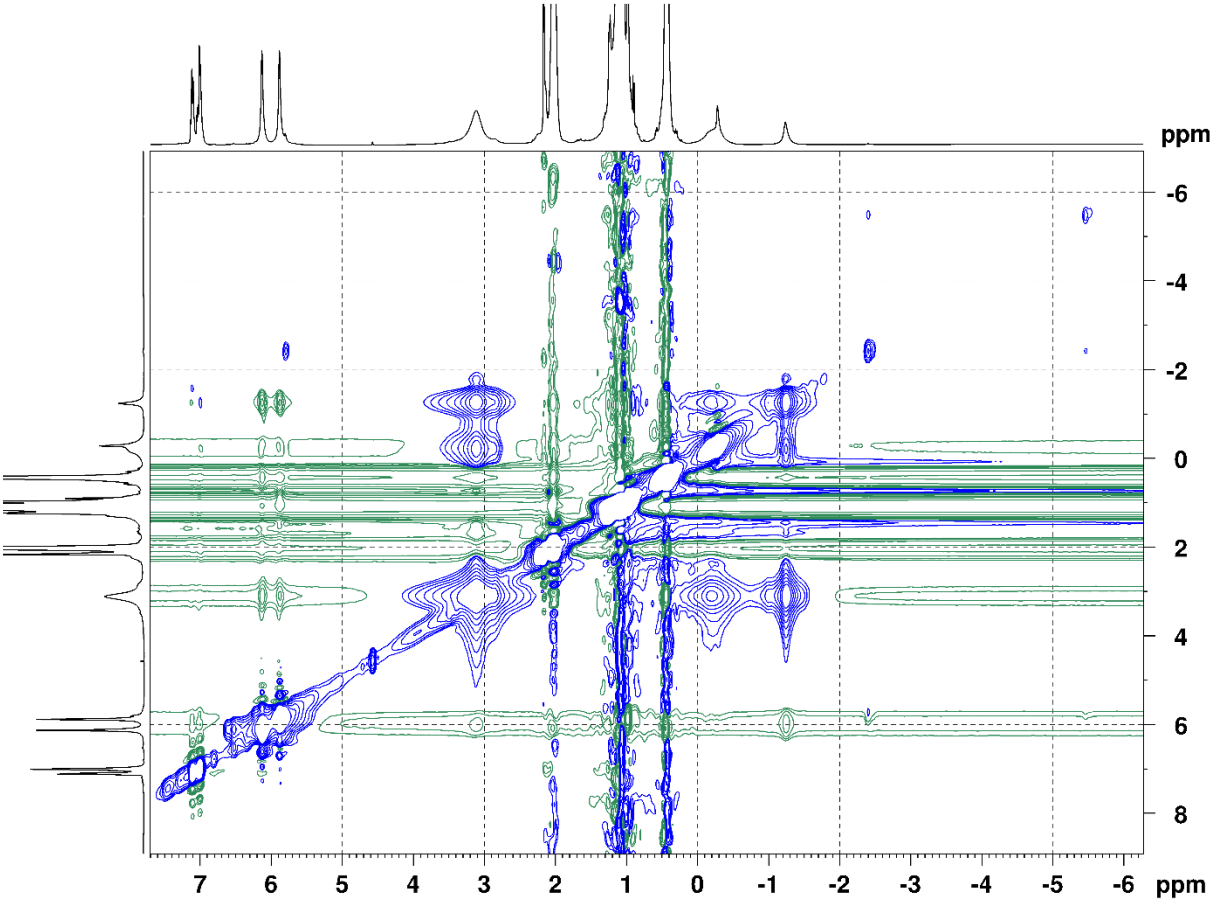

Figure S32. ^1H NMR of system $Me_2CInd_2ZrCl_2$ (**1e**) − $HAlBu^i_2$ (1:4) in C_7D_8 (298 K).

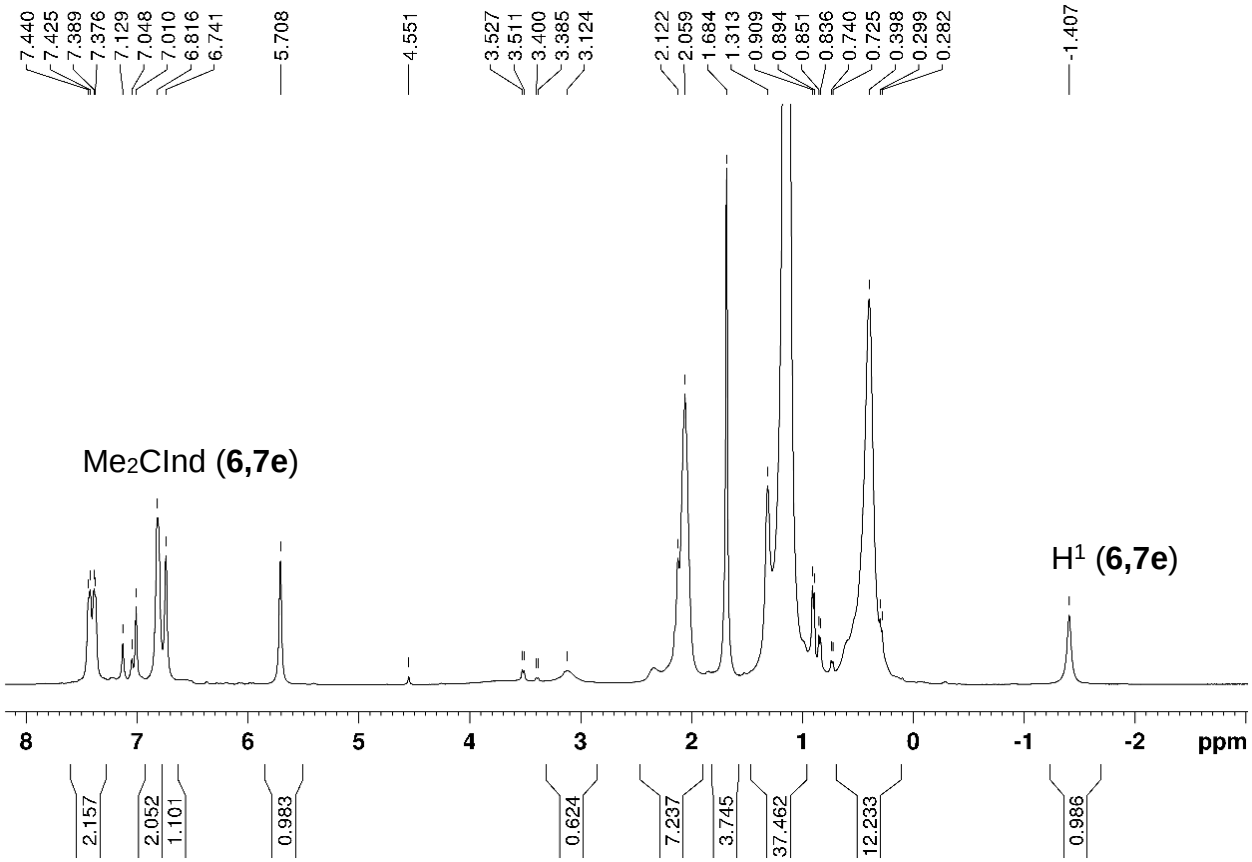

Figure S33. ^{13}C NMR of system $Me_2CInd_2ZrCl_2$ (**1e**) − $HAlBu^i_2$ (1:4) in C_7D_8 (298 K).

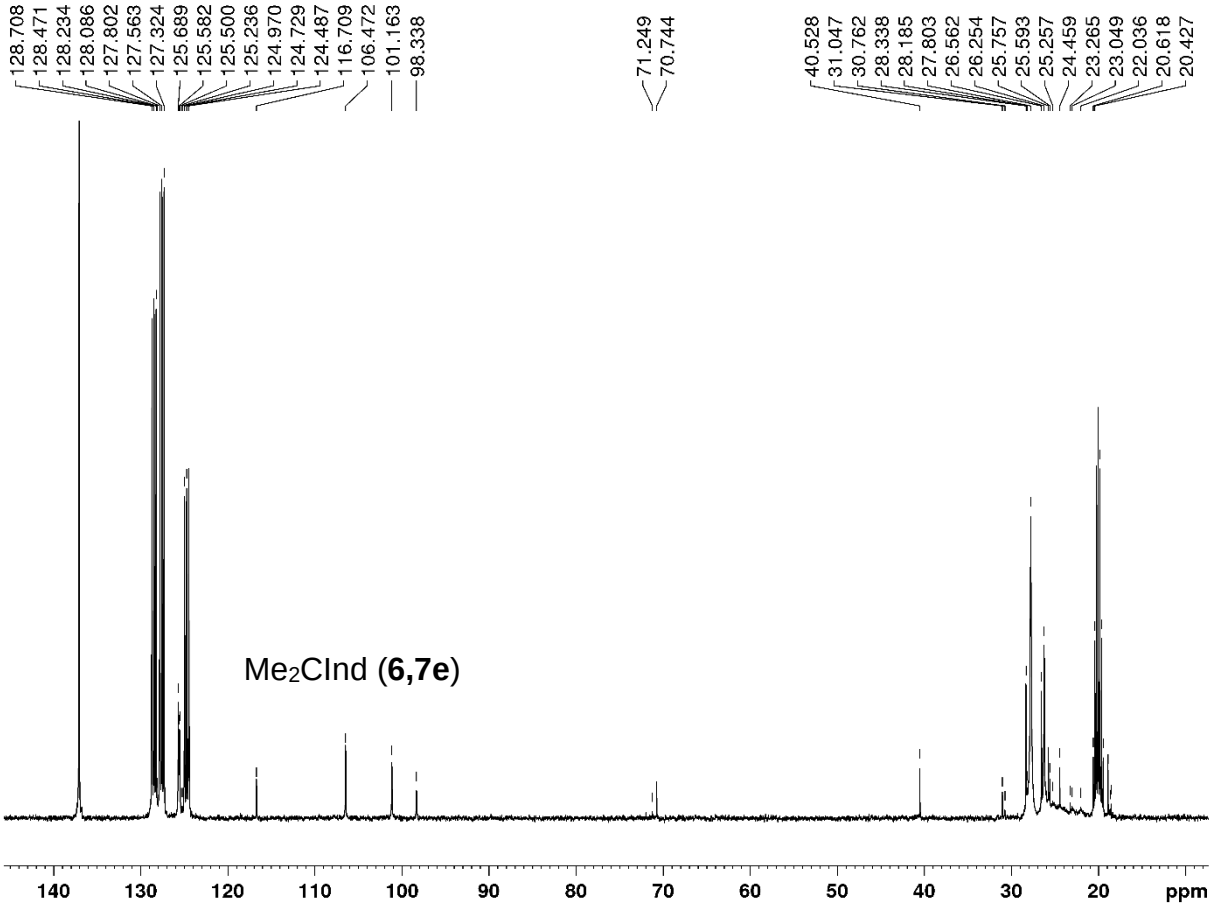

Figure S34. COSY HH of system $Me_2CInd_2ZrCl_2$ (**1f**) − $HAlBu^i_2$ (1:4) in C_7D_8 (280 K).

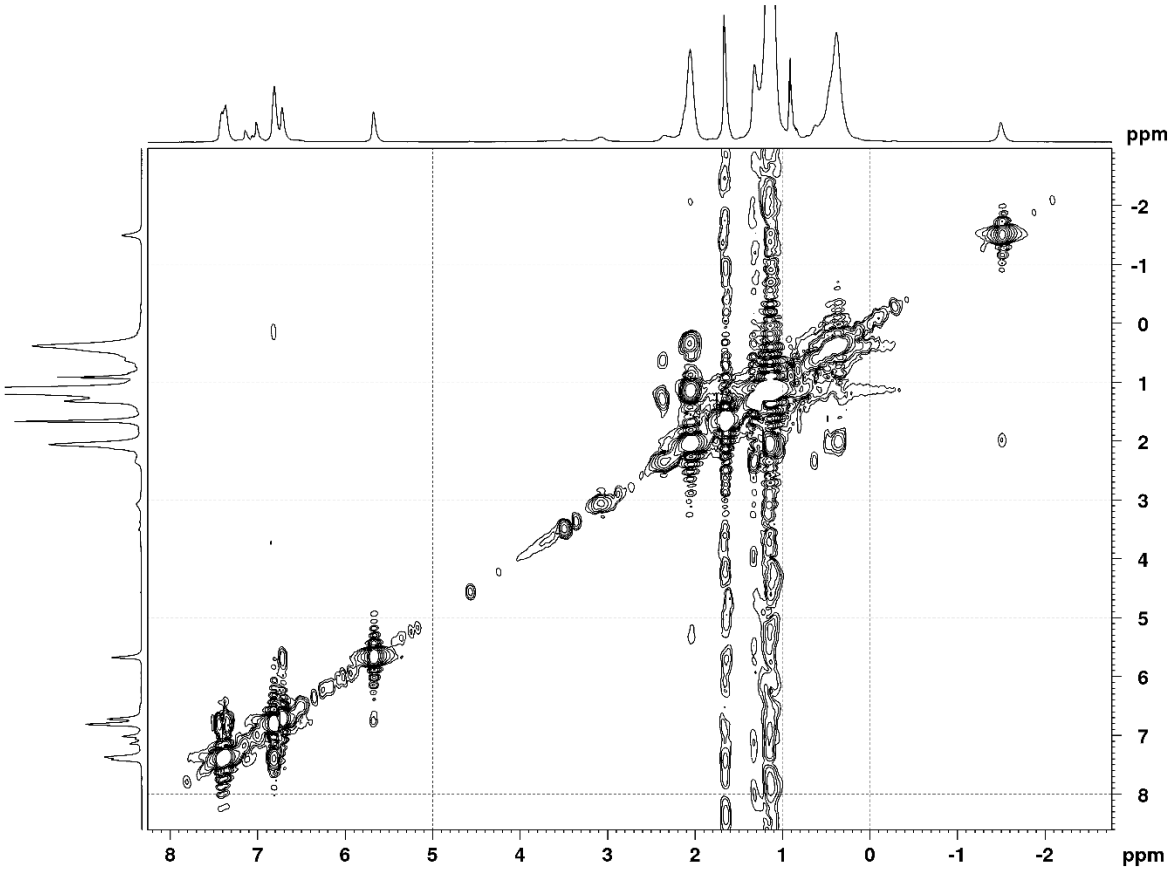

Figure S35. NOESY of system $Me_2CInd_2ZrCl_2$ (**1e**) − $HAlBu^i_2$ (1:4) in C_7D_8 (298 K).

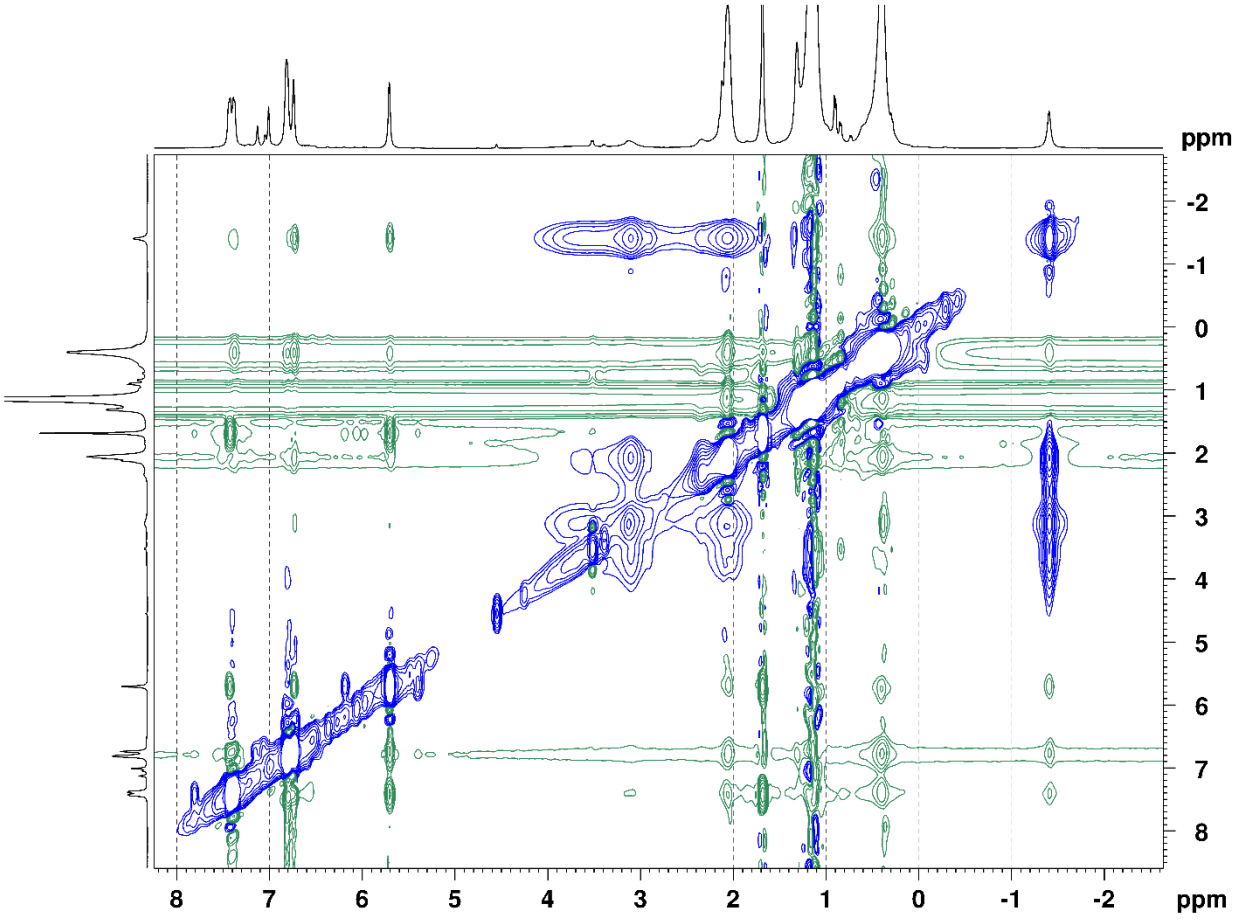

Figure S36. ^1H NMR of system $Me_2CInd_2ZrCl_2$ (**1e**) − $HAlBu^i_2$ – MMAO-12 (1:4:8) in C_7D_8 (298 K).

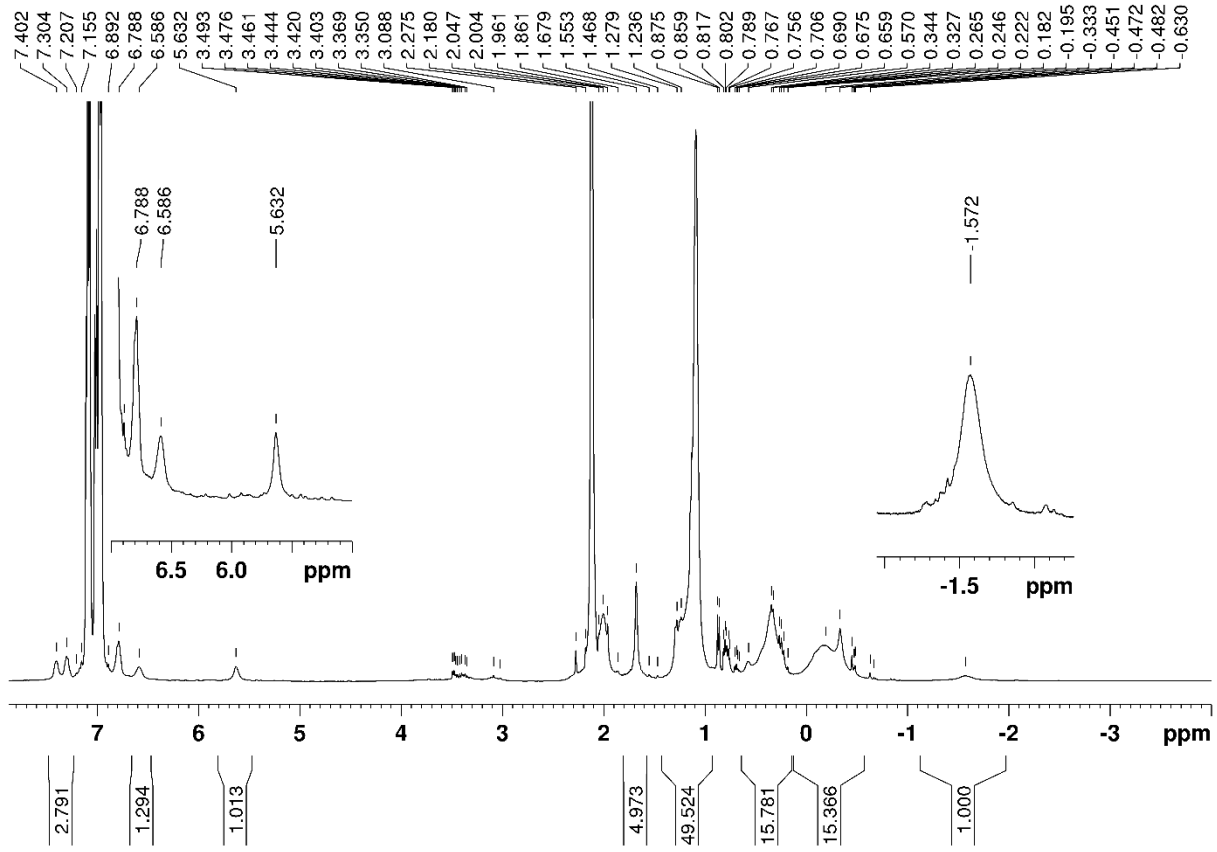

Figure S37. NOESY of system $Me_2CInd_2ZrCl_2$ (**1e**) − $HAlBu^i_2$ – MMAO-12 (1:4:8) in C_7D_8 (298 K).

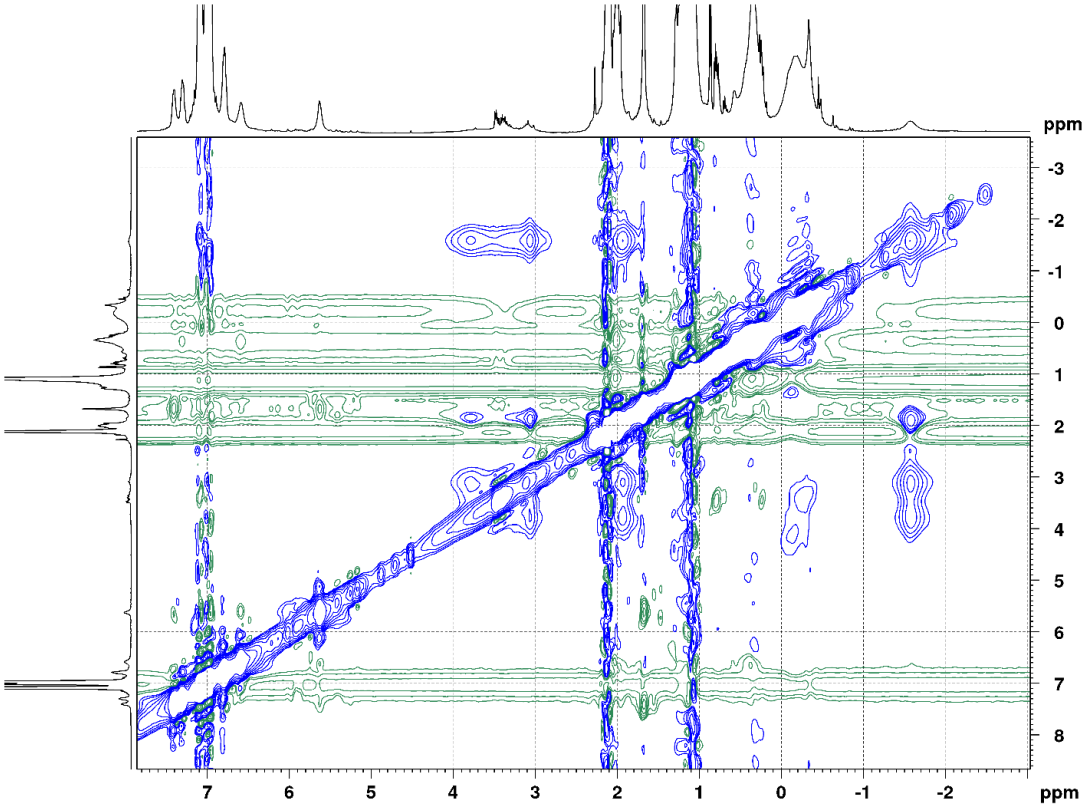

Figure S38. ^{13}C NMR of products obtained after the addition of hexene-1 to the system $(CpMe)_2ZrCl_2$ (**1c**) − $HAlBu^i_2$ – MMAO-12 (1:4:11) in C_7D_8, 333 K, 10 min.

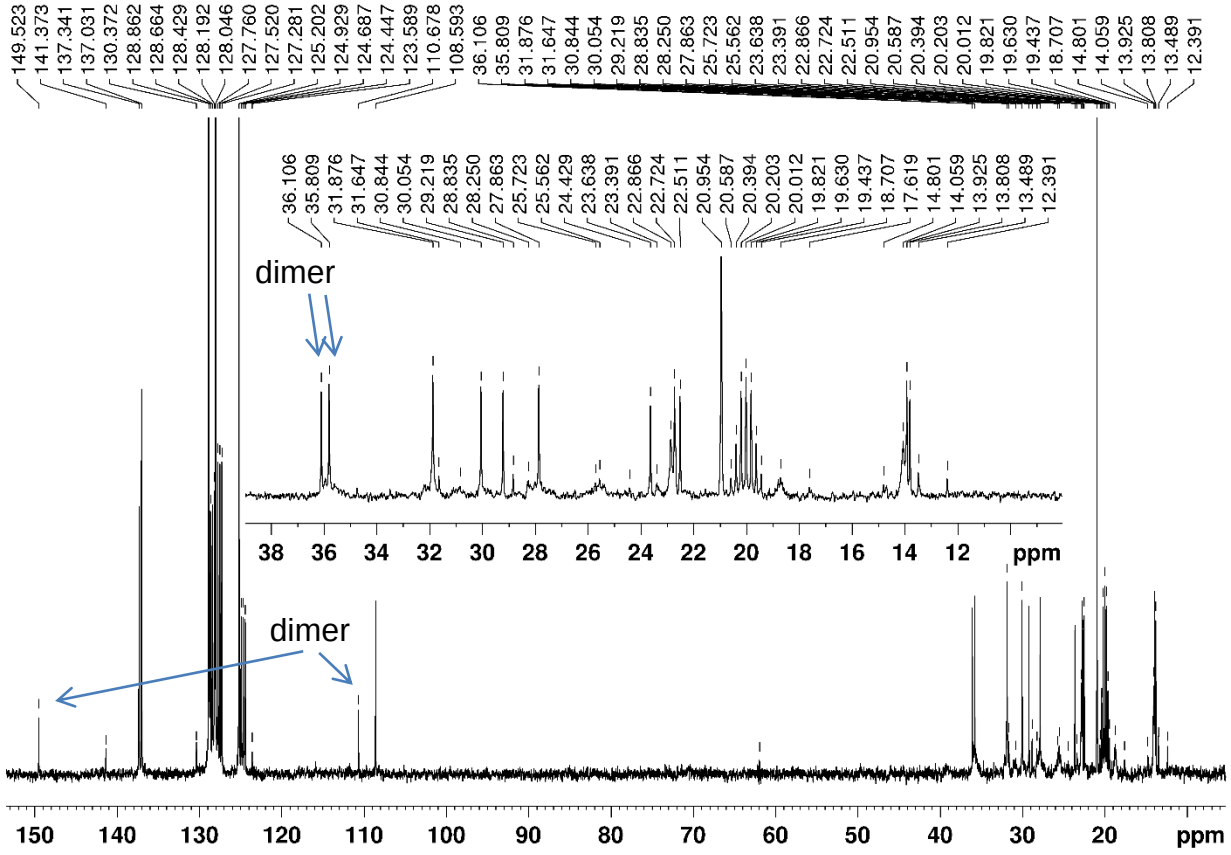

Figure S39. ^{13}C NMR of products obtained after the addition of hexene-1 to the system $Me_2CInd_2ZrCl_2$ (**1e**) − $HAlBu^i_2$ – MMAO-12 (1:4:8) in C_7D_8, 333 K, 10 min.