Bimetallic Zr,Zr- Hydride Complexes in Zirconocene Catalysed Alkene Dimerization

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Supporting Information

Figure S1. Effect of OAC structure on product yield in the system $[Cp_2ZrH_2]_2$−$ClAlR_2$−MMAO-12− 1-hexene (1:3:30:100, 20°C):
(a) - $ClAlMe_2$; (b) - $ClAlEt_2$; (c) $ClAlBu^i_2$.

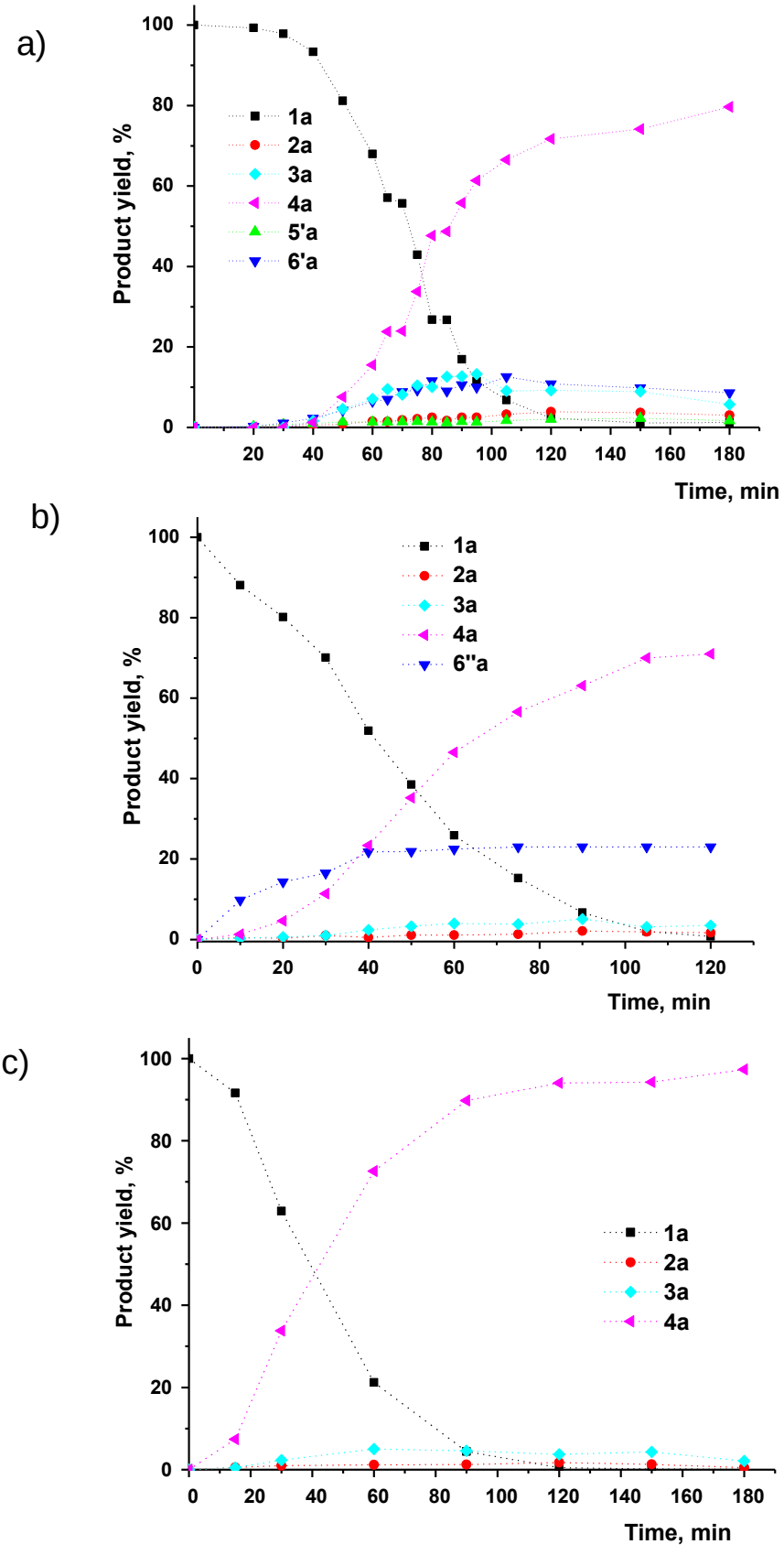


Figure S2. ^{1}H NMR of system Cp_2ZrCl_2 − $AlBu^{i}_3$ (1:5) in C_7D_8 (240 K).

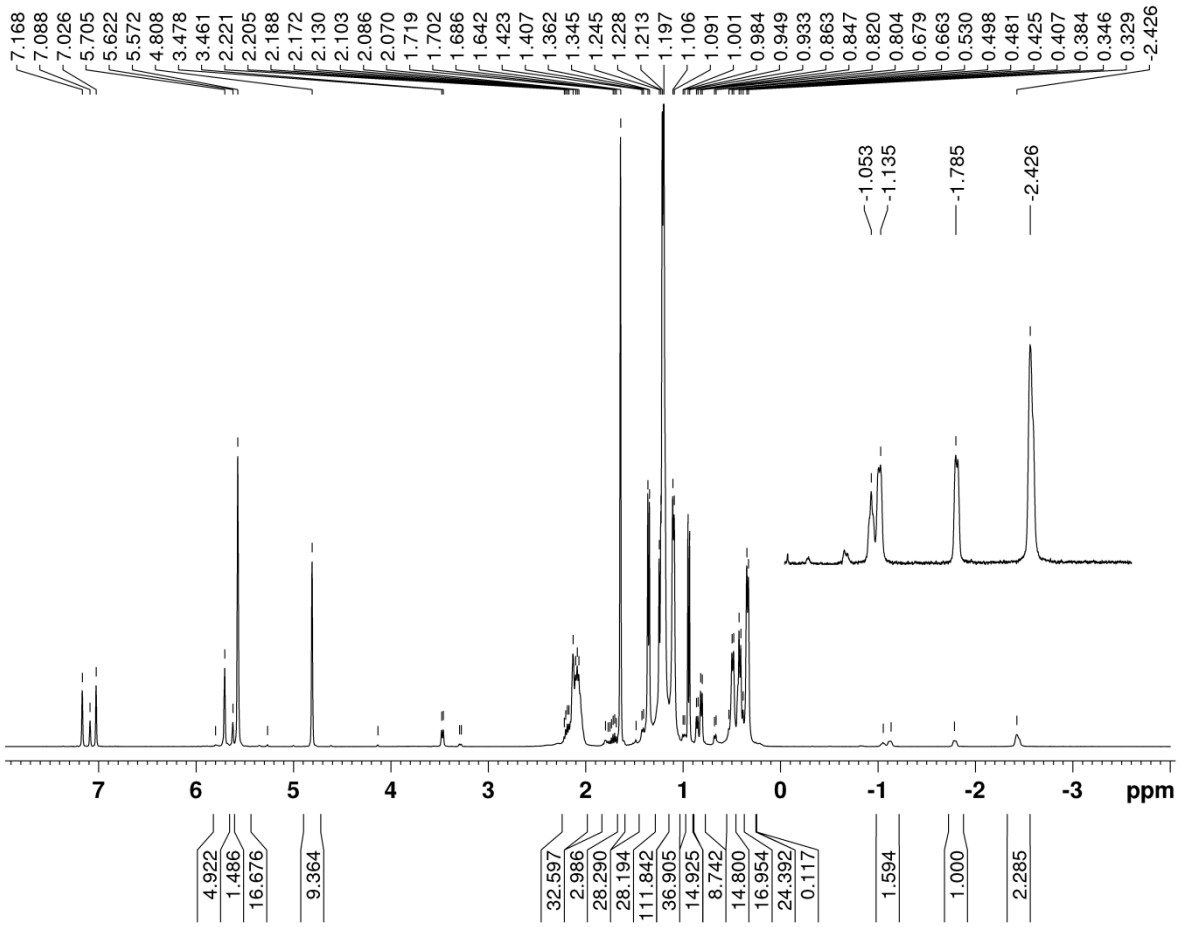


Figure S3. ^{1}H NMR of system Cp_2ZrCl_2 − $AlBu^{i}_3$ (1:5) in C_7D_8 (298 K).

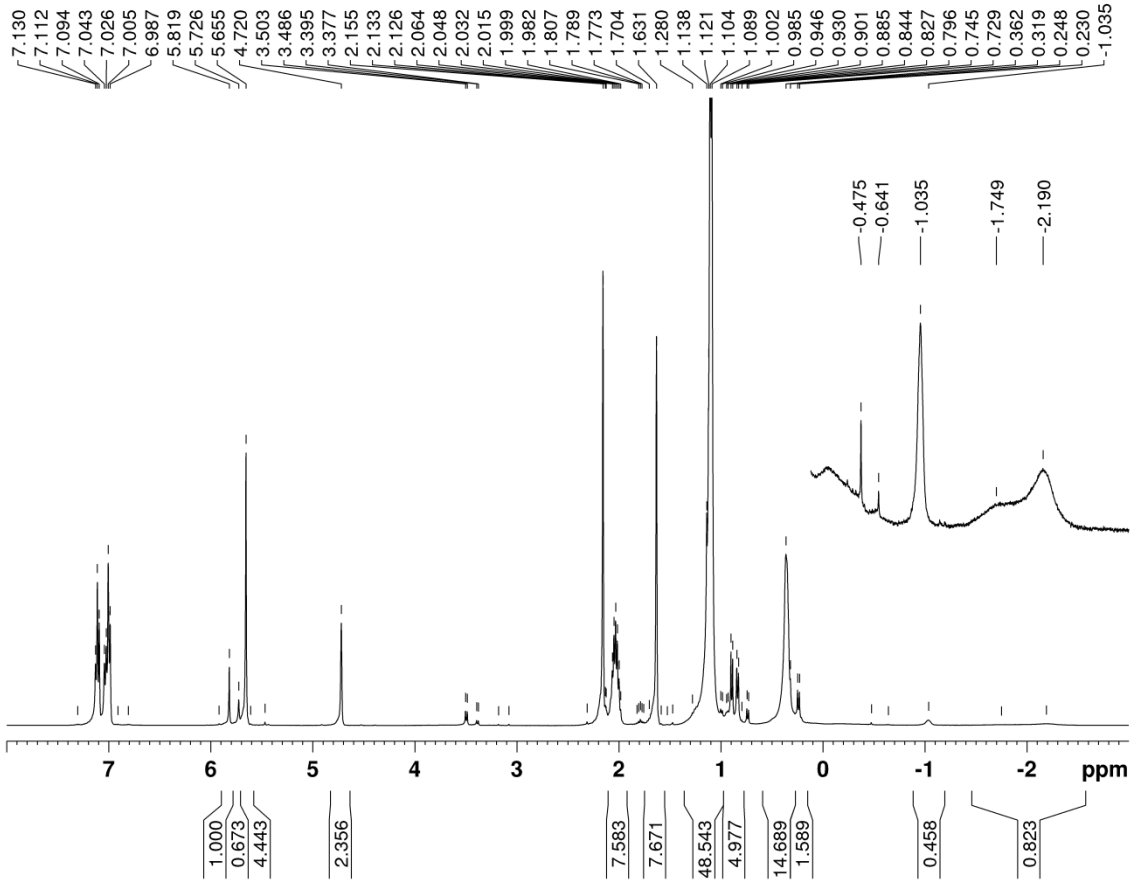


Figure S4. ^{1}H NMR of system Cp_2ZrCl_2 − $AlBu^{i}_3$ – MMAO-12 (1:5:12) in C_7D_8 (298 K).

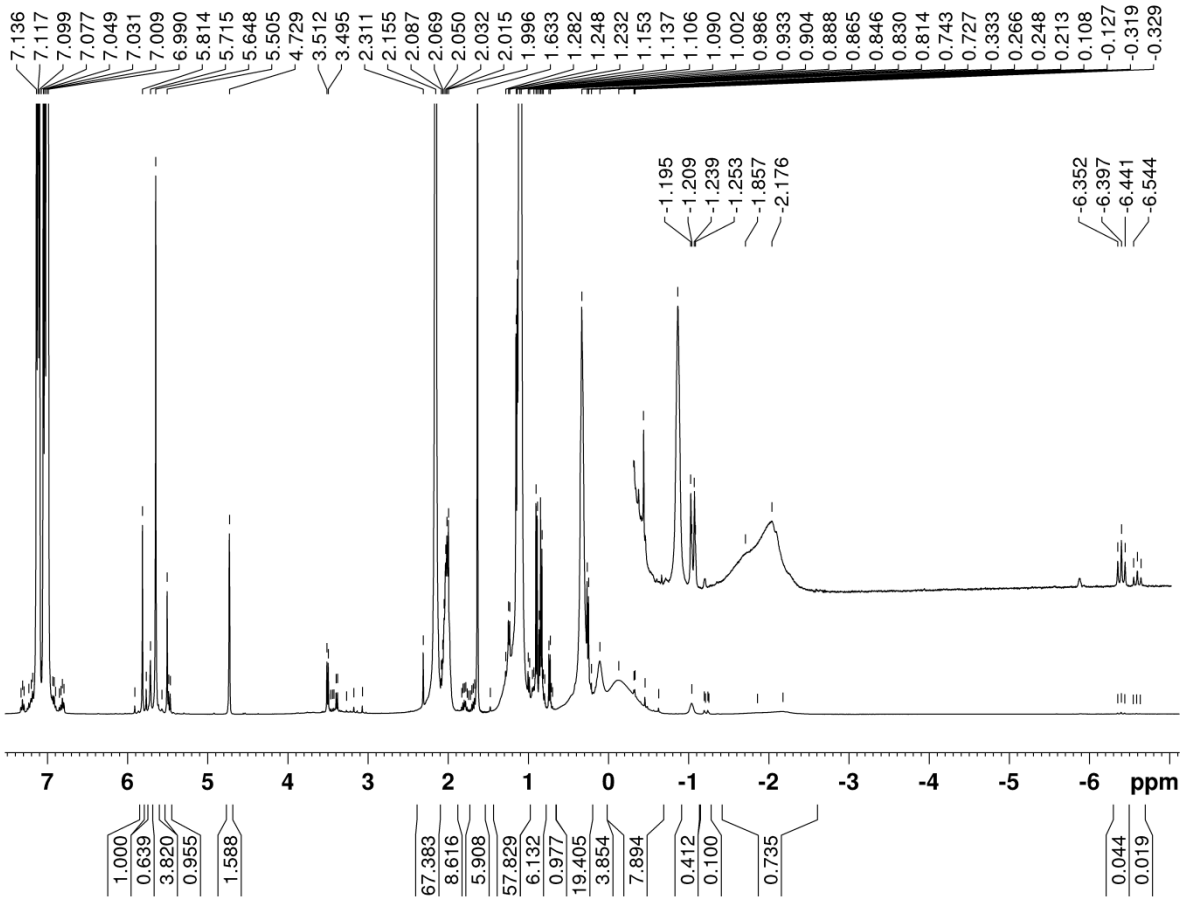


Figure S5. COSY HH of system Cp_2ZrCl_2 − $AlBu^{i}_3$ – MMAO-12 (1:5:12) in C_7D_8 (298 K).

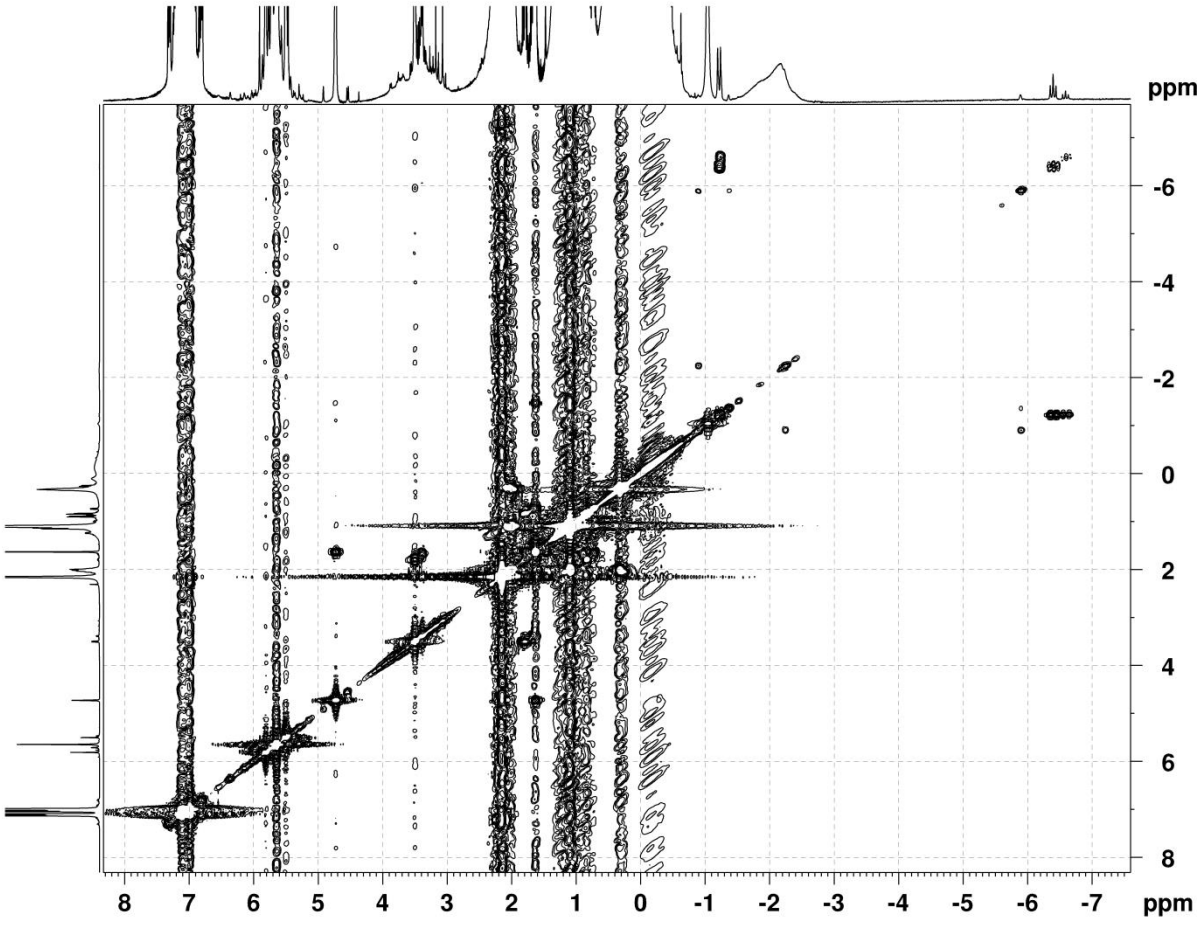


Figure S6. NOESY of system Cp_2ZrCl_2 − $AlBu^i_3$ – MMAO-12 (1:5:12) in C_7D_8 (298 K).

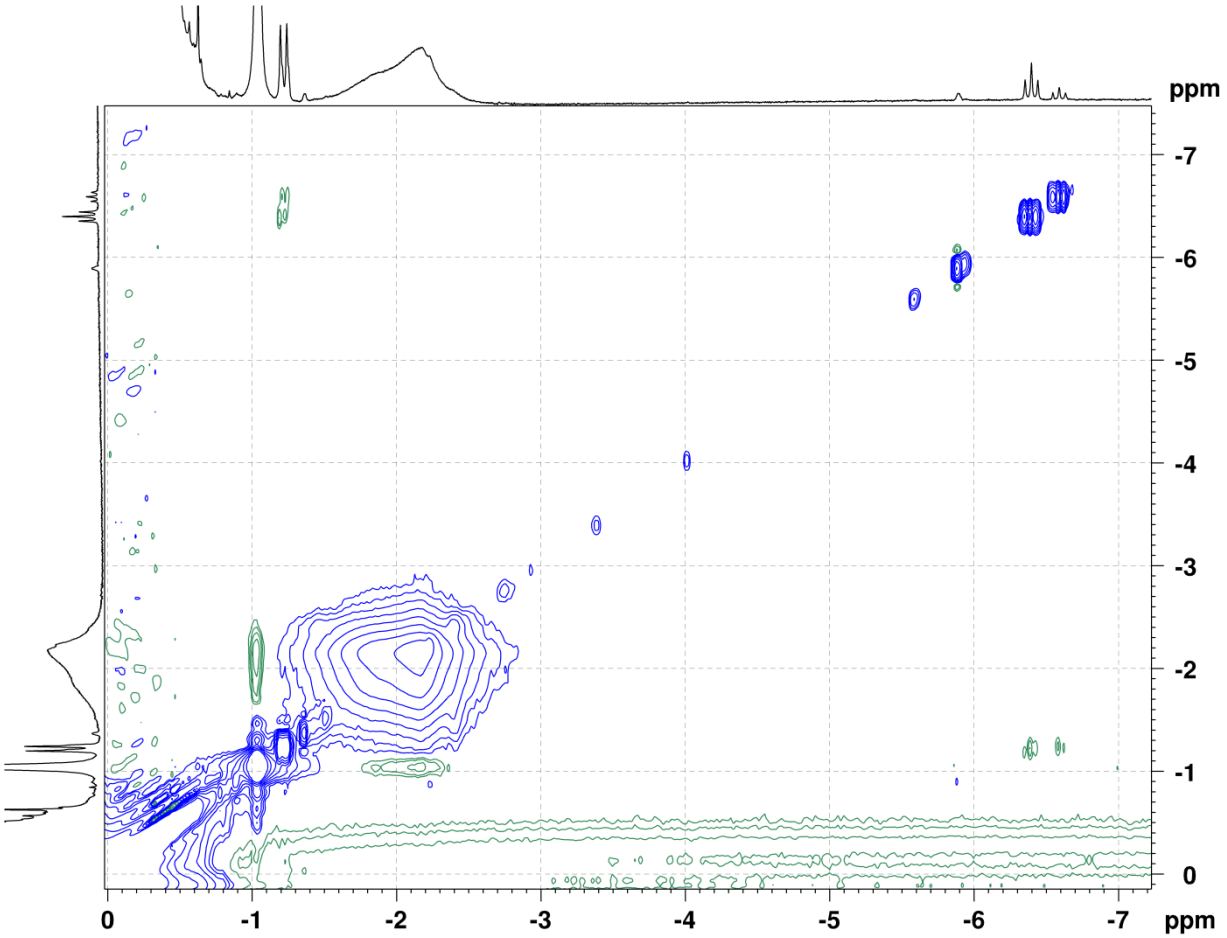


Figure S7. ^{1}H NMR of system Cp_2ZrCl_2–$HAlBu^i_2$–MMAO-12 in C_7D_8 (T= 298 K): a) [Zr]:[Al]:[Al_{MAO}]= 1:1.5:0; b) [Zr]:[Al]:[Al_{MAO}]= 1:1.5:1.5; c) [Zr]:[Al]:[Al_{MAO}]= 1:1.5:3.

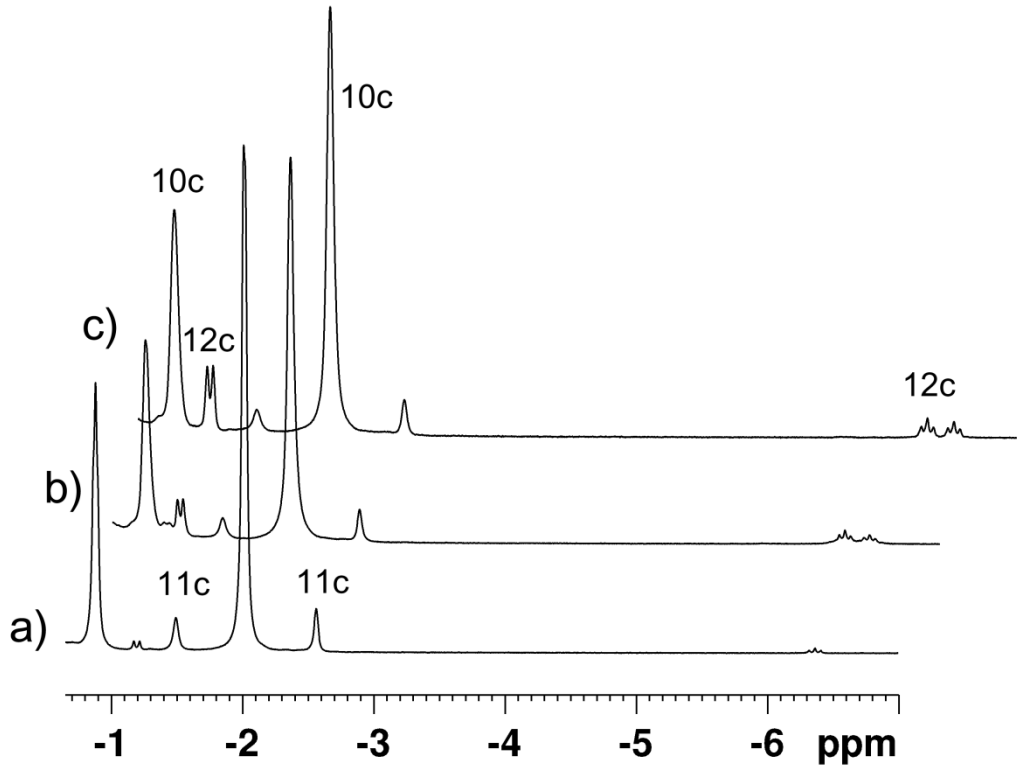


Figure S8. ^{1}H NMR of system Cp_2ZrCl_2 − $HAlBu^i_2$ (1:2) in C_7D_8.

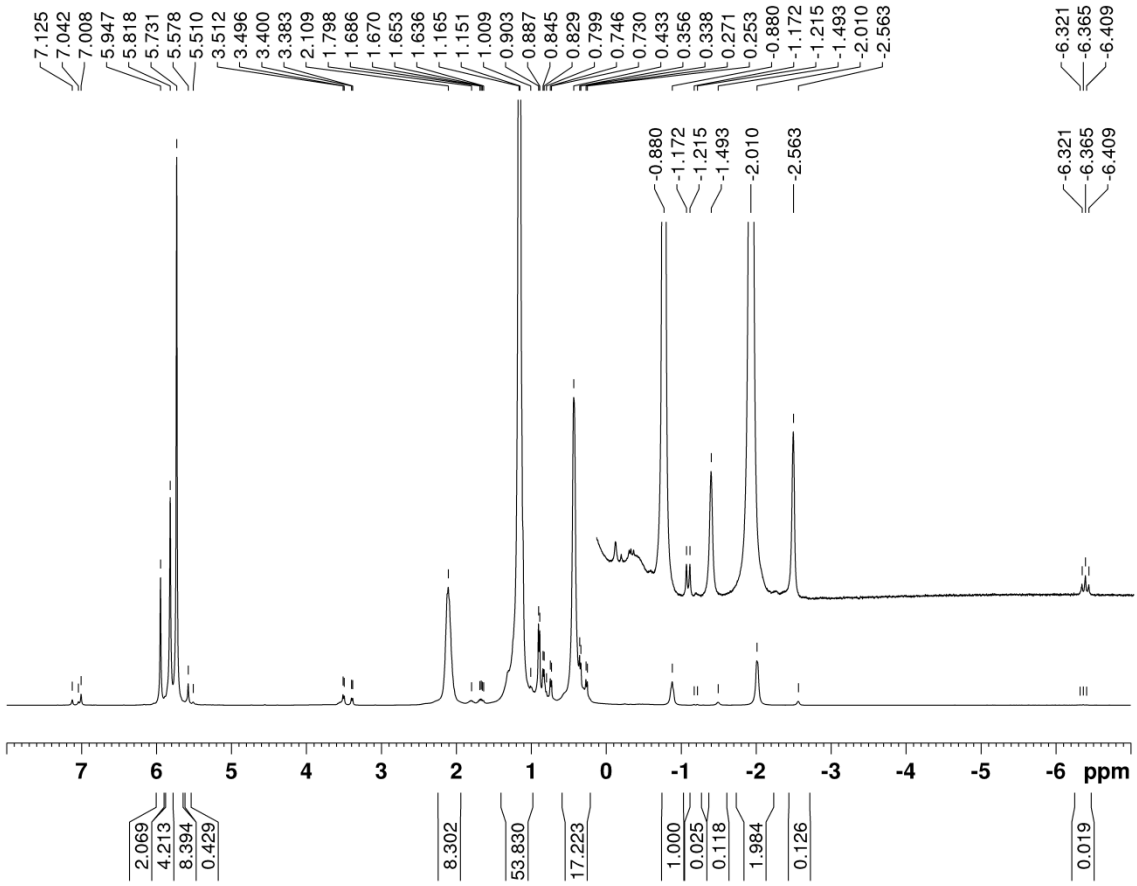


Figure S9. ^{1}H NMR of system Cp_2ZrCl_2 − $HAlBu^i_2$ – MMAO-12 (1:1.5:3) in C_7D_8.

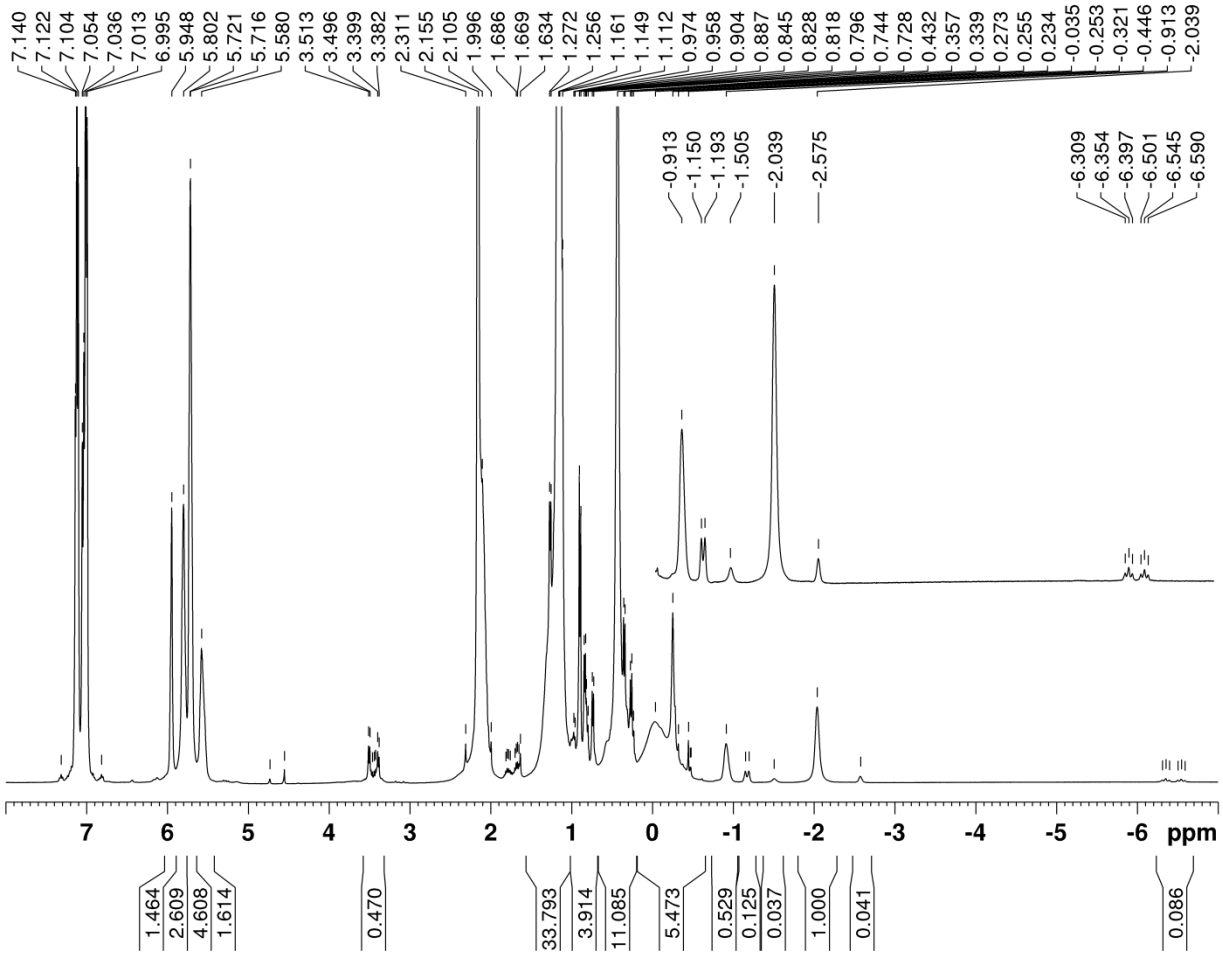


Figure S10. ^{1}H NMR of system $[Cp_2ZrH_2]_2$ − $ClAlMe_2$ (1:3) in C_7D_8.

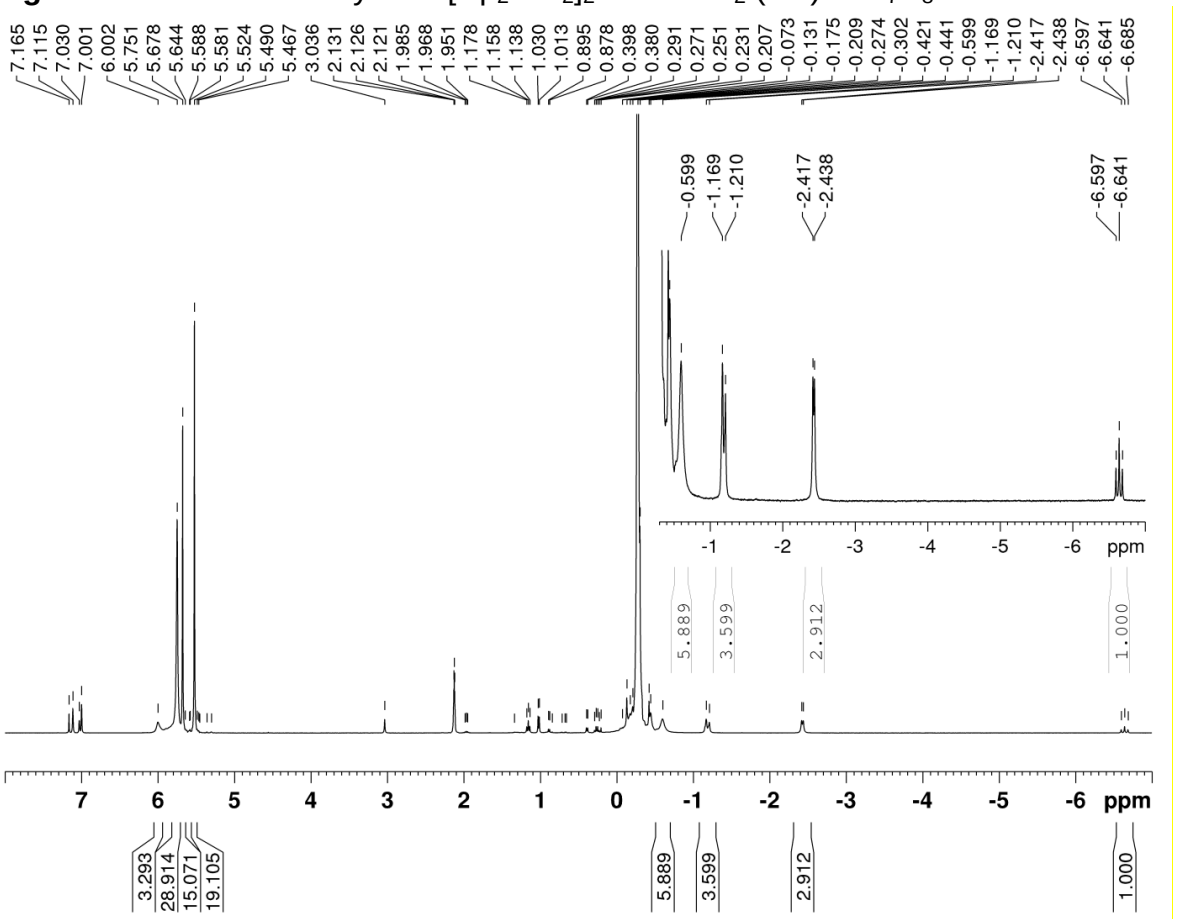


Figure S11. COSY HH of system $[Cp_2ZrH_2]_2$ − $ClAlMe_2$ (1:3) in C_7D_8.

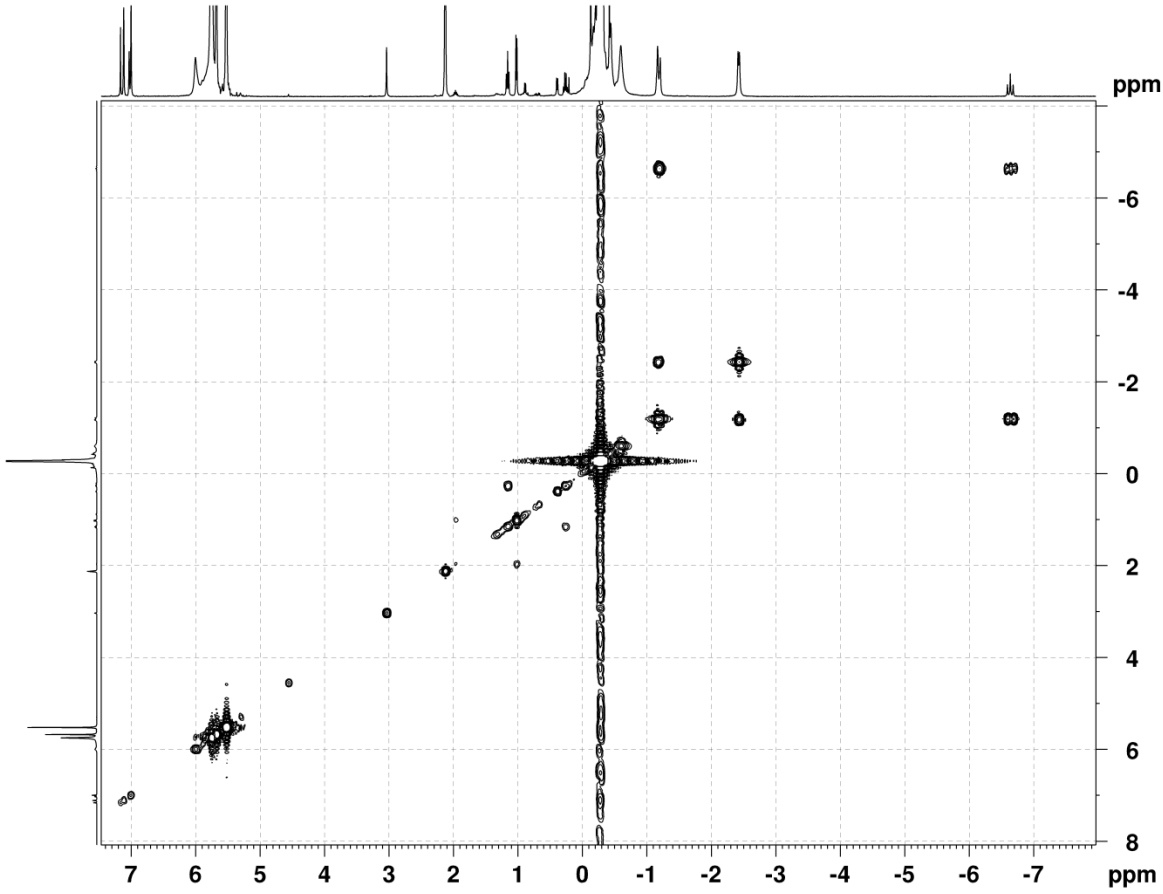


Figure S12. ^{13}C NMR of system $[Cp_2ZrH_2]_2$ − $ClAlMe_2$ (1:3) in C_7D_8.

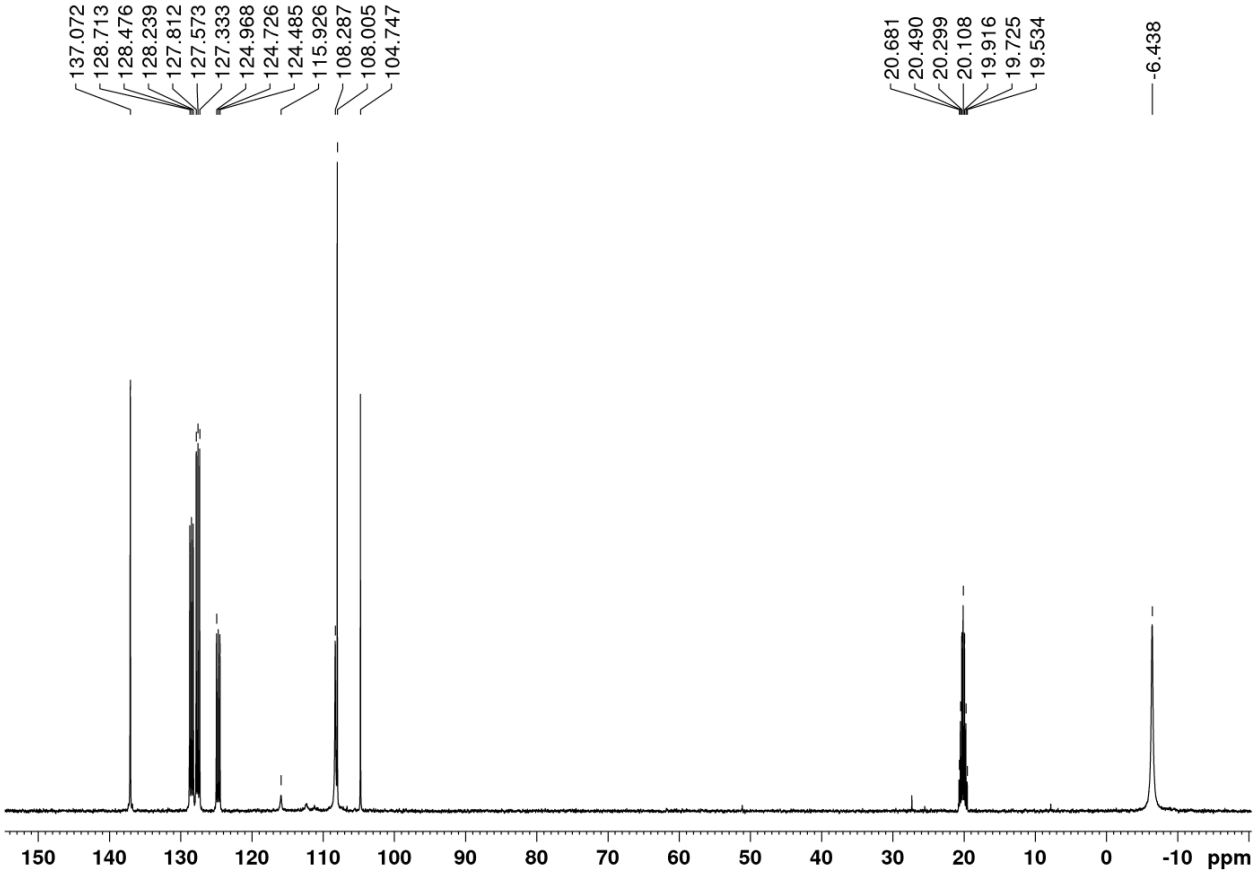


Figure S13. HSQC of system $[Cp_2ZrH_2]_2$ − $ClAlMe_2$ (1:3) in C_7D_8.

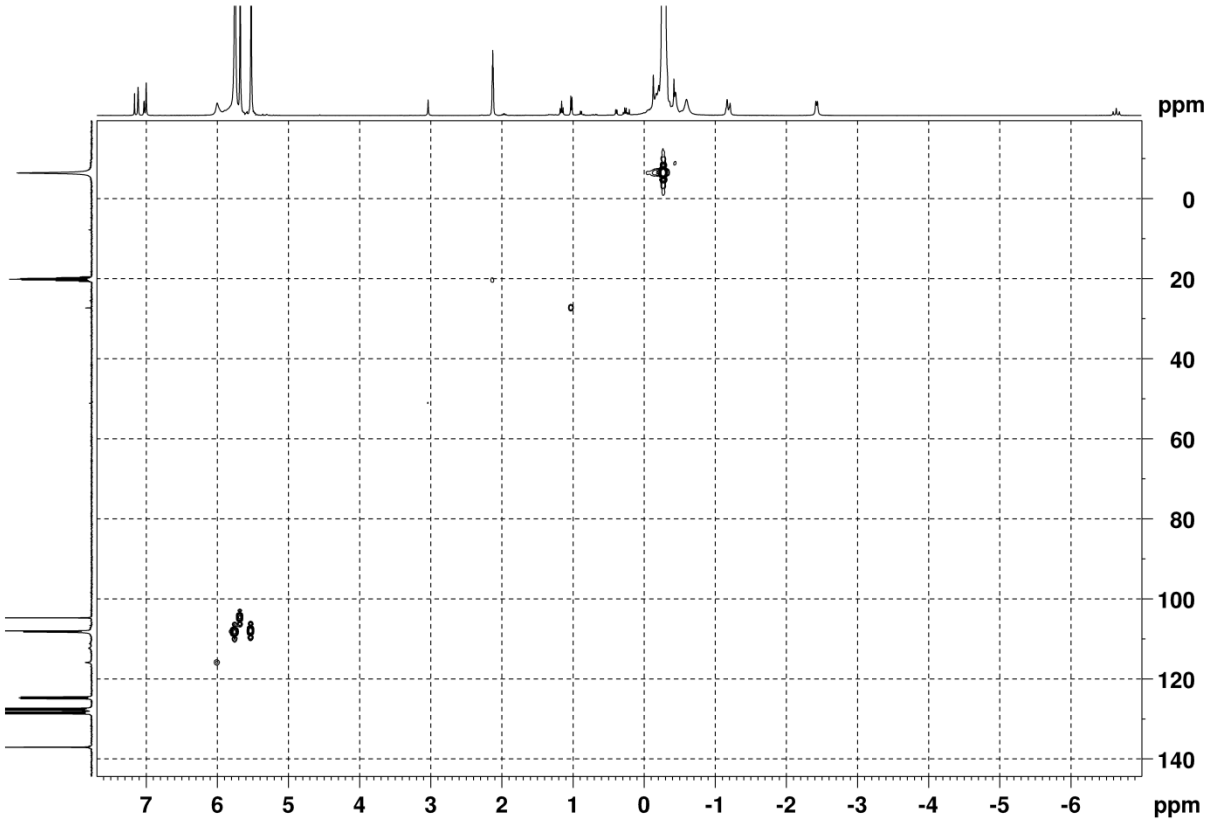


Figure S14. ^{1}H NMR of system $[Cp_2ZrH_2]_2$ − $ClAlMe_2$ – MMAO-12 (1:3:6) in C_7D_8.

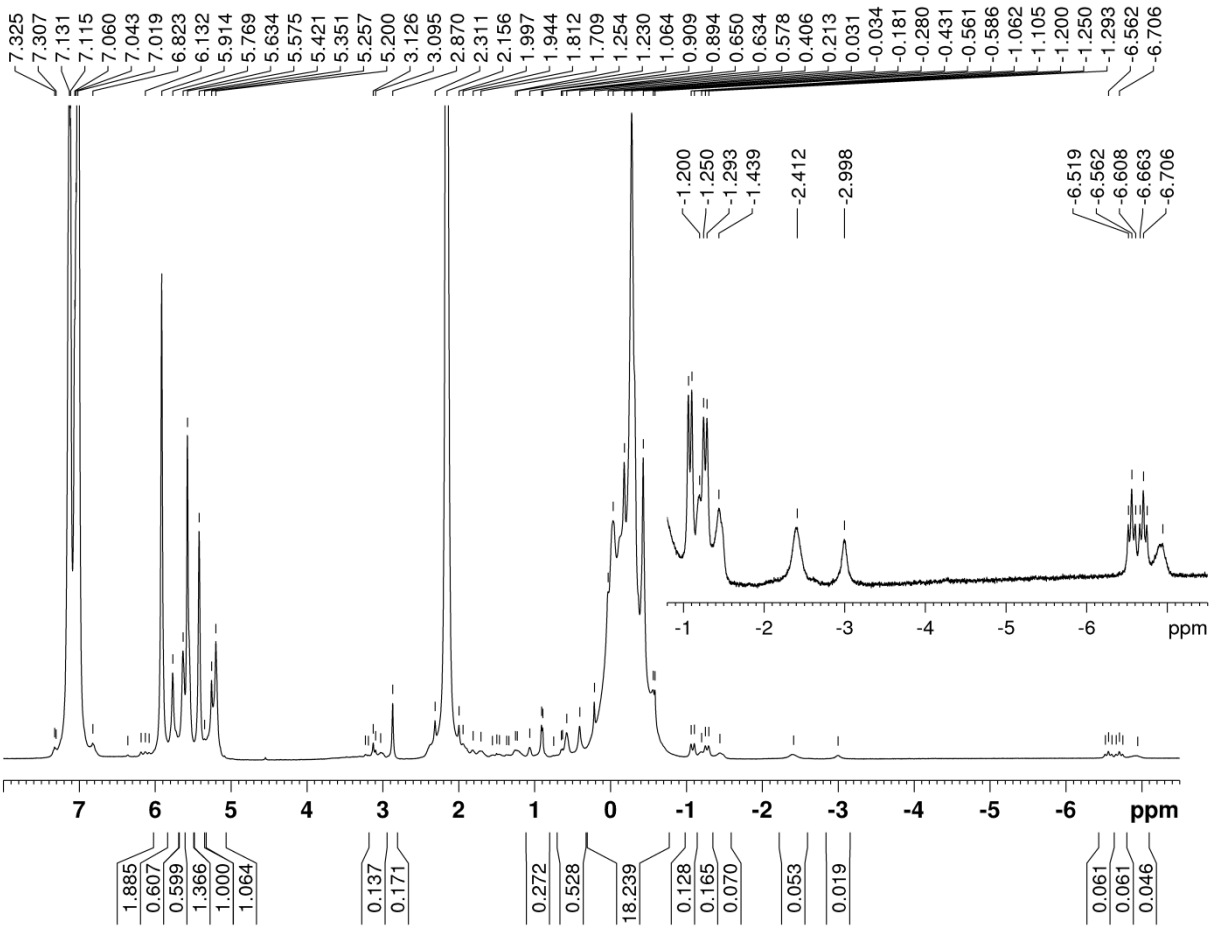


Figure S15. DOSY of system $[Cp_2ZrH_2]_2$−$ClAlMe_2$–MMAO-12 (1:3:6) in C_7D_8 (T=299.3 K).

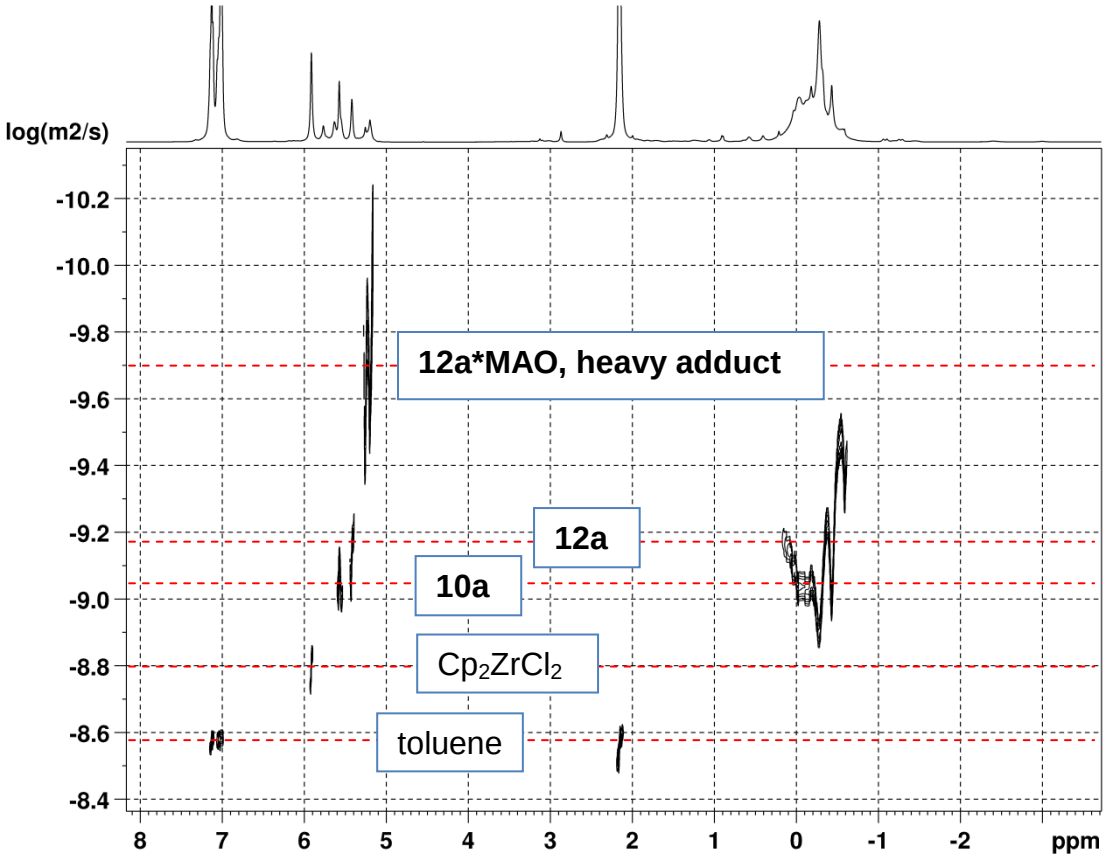


Figure S16. COSY of system $[Cp_2ZrH_2]_2$−$ClAlMe_2$–MMAO-12 (1:3:6) in C_7D_8.

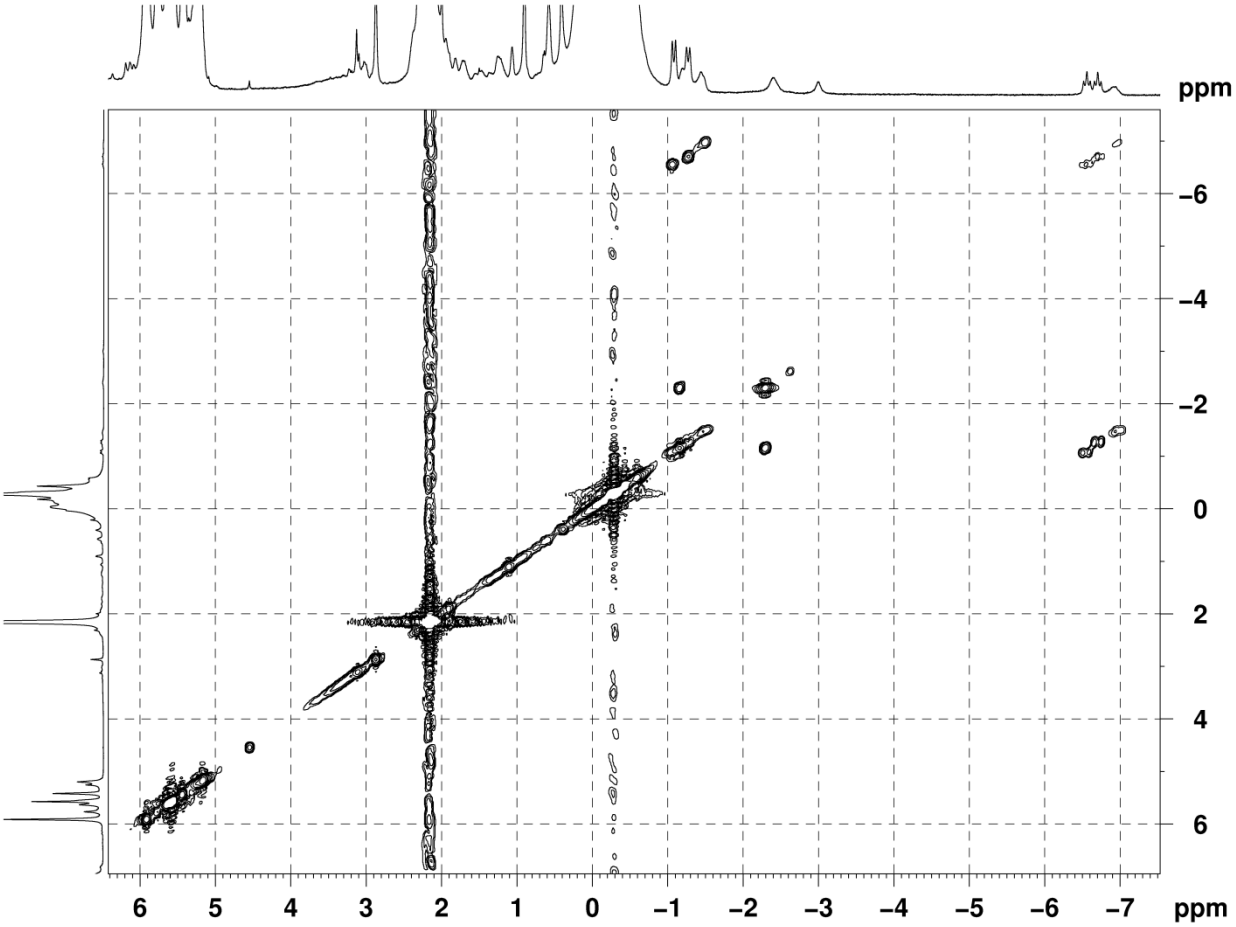


Figure S17. NOESY of system $[Cp_2ZrH_2]_2$−$ClAlMe_2$–MMAO-12 (1:3:6) in C_7D_8.

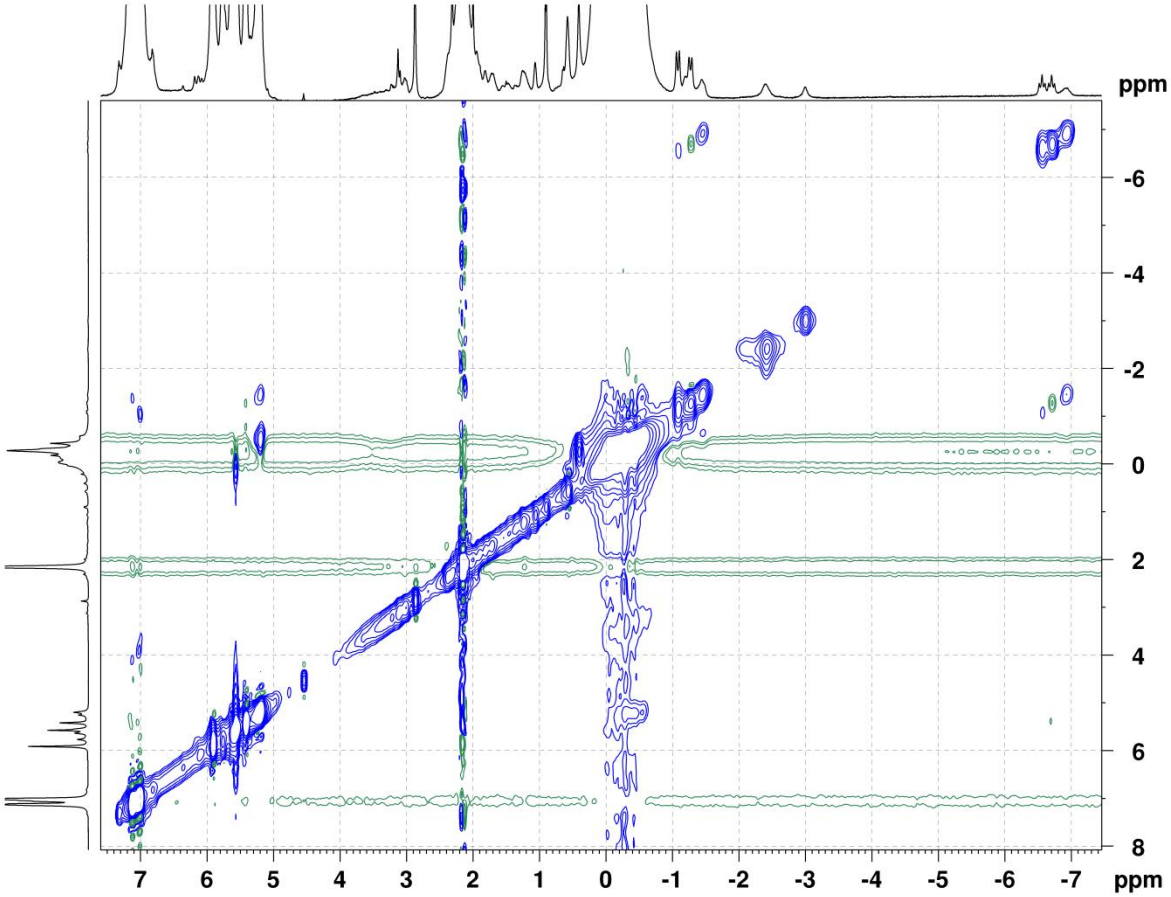


Figure S18. ^{1}H NMR of system $[Cp_2ZrH_2]_2$ − $ClAlEt_2$ (1:3) in C_7D_8.

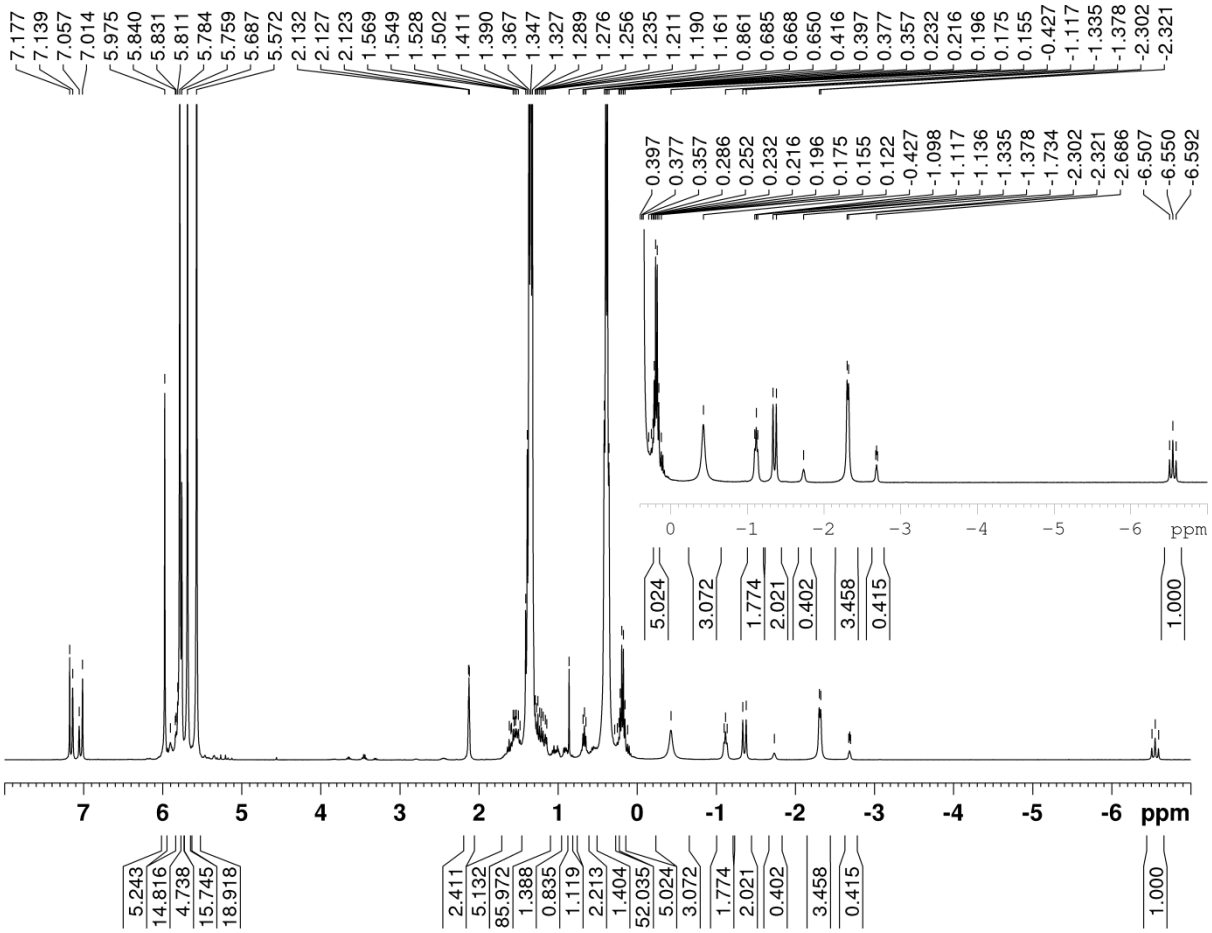


Figure S19. NMR monitoring of system $[Cp_2ZrH_2]_2$− $ClAlBu^{i}_2$ – 1-hexene (1:2.6:(0.7-2.4)) in C_7D_8, intensity of upfield signals is increased.

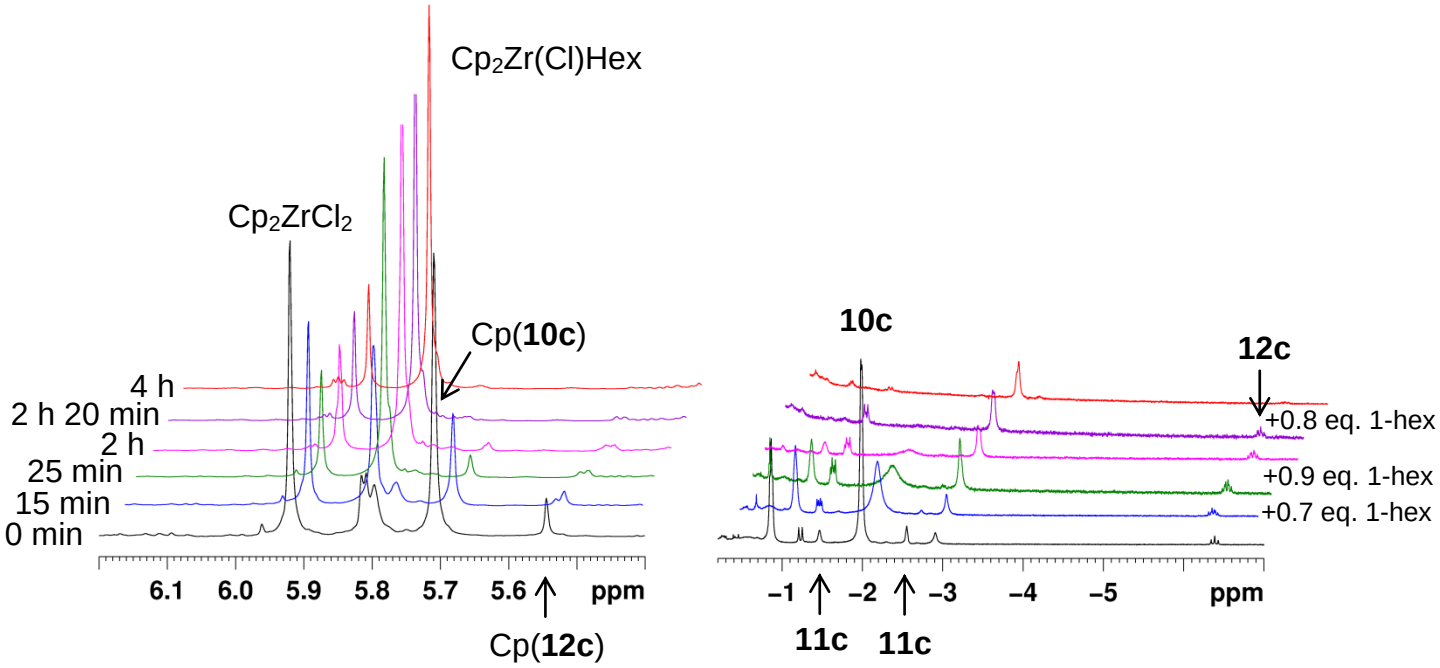


Figure S20. ^{13}C NMR of system $[Cp_2ZrH_2]_2$ − $ClAlBu^i_2$ – 1-hexene (1:2.6:(0.7-2.4)) in C_7D_8 (end of reaction).

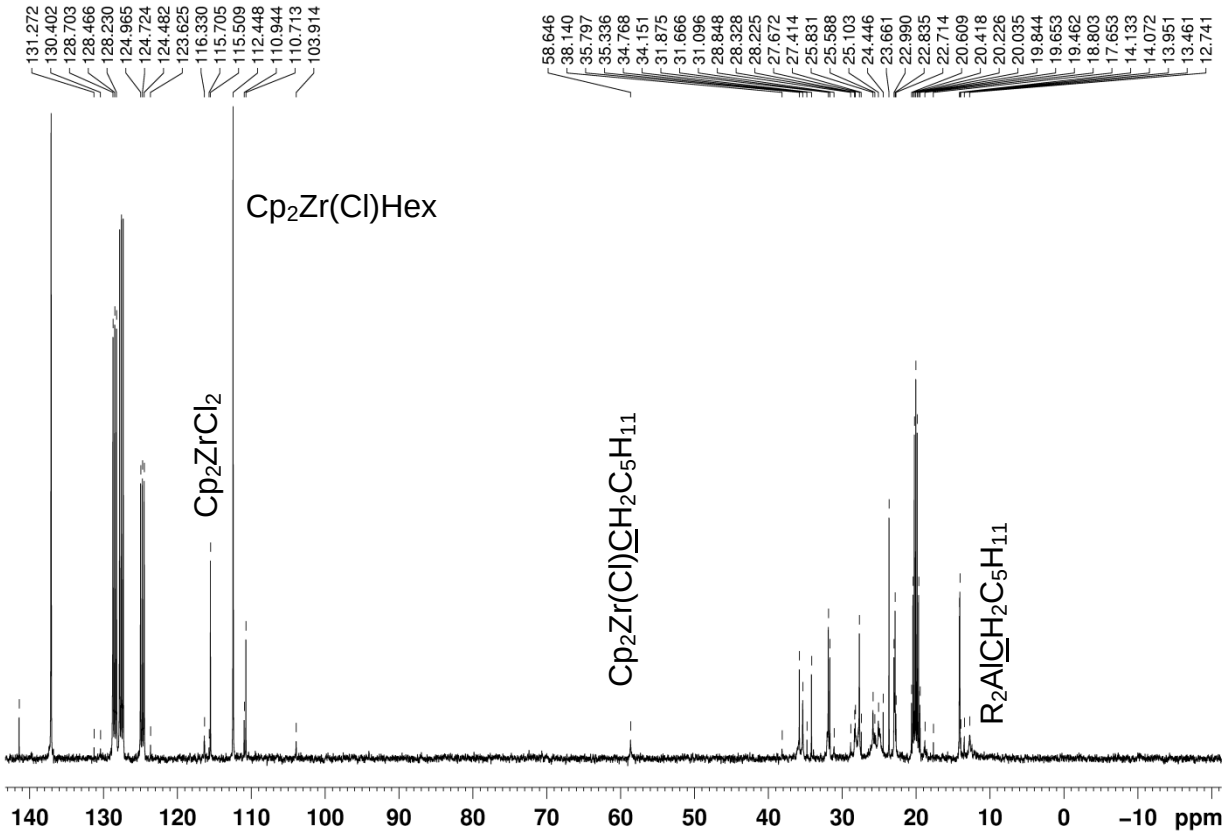
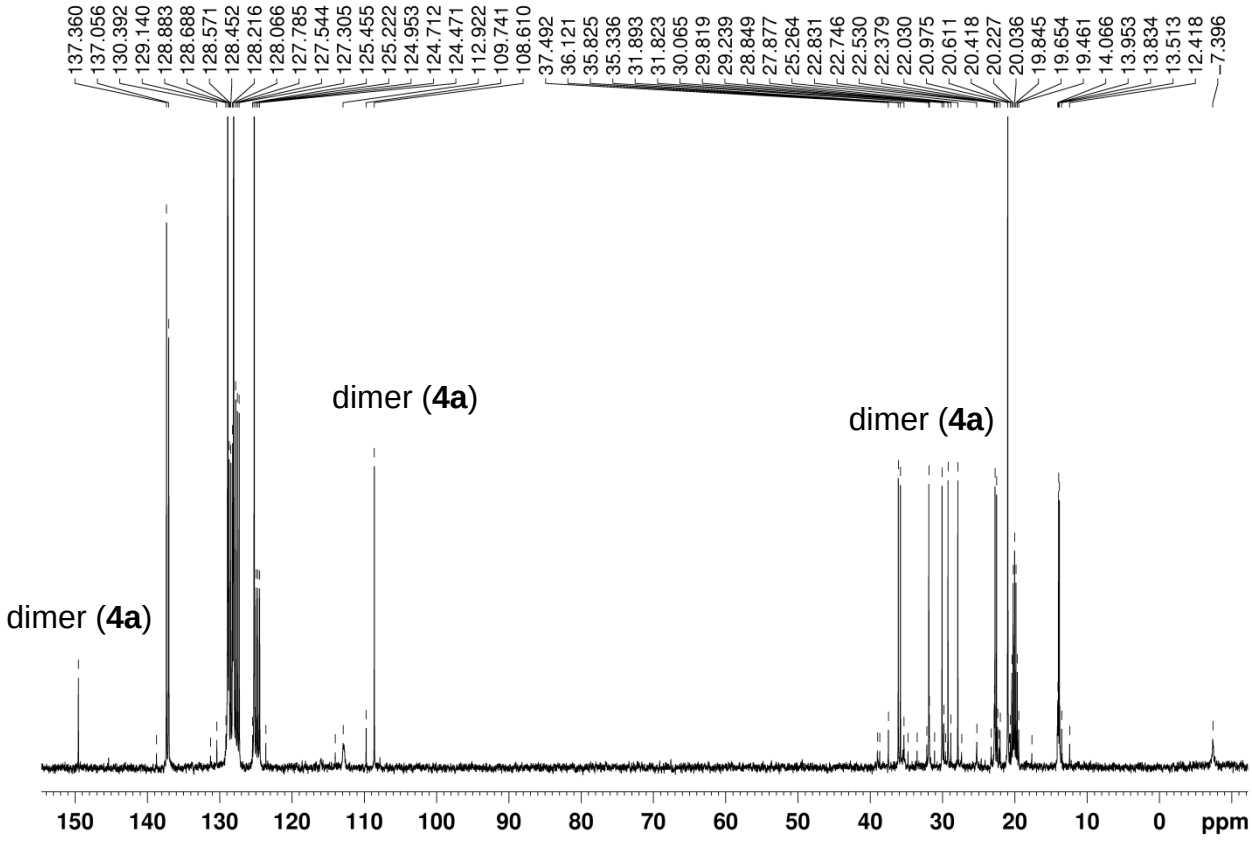


Figure S21. ^{13}C NMR of system $[Cp_2ZrH_2]_2$ − $ClAlMe_2$ – MMAO-12 – 1-hexene in C_7D_8 (end of reaction).



GC-MS analysis of products

Before each series of mass spectral analysis, calibration was performed using alkene-dimer mixtures with various molar concentrations to determine response factors (RF). Response factors of dimers were calculated as RF(dimer)= Slope(1-alkene)/Slope(dimer), where Slope(1-alkene) was found from the dependence Peak area (1-alkene) – Concentration (1-alkene), and Slope(dimer) from the dependence Peak area (dimer) – Concentration (dimer). 1-Alkenes were used as a standards with RF=1. Response factors of low molecular weight products **2-D**, **5-D** and **6** were taken as 1 as well. Thus, product yields were determined via peak areas multiplied by response factors. RFs of trimers were taken as RFs of dimers.

Figure S22. Example of GC-MS of products obtained in the system Cp_2ZrCl_2 – $AlMe_3$ – MMAO-12– 1-hexene (Table 1, entry 18)