Electronic Supplementary Information

Tri- and tetra-dentate imine vanadyl complexes: Synthesis, structure and ethylene polymerization/ring opening polymerization capability

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Figure S1. Stacking of 2 along the *b* axis.



Figure S2. CAMERON representation of 2^{*l*} showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): V1 − O1 1.8880(18), V1 − O(2) 1.629(2), V1 − O(3) 1.623(2), V1 − N1 2.185(2), V1 − N2 2.161(2); O1 − V1 − N1 155.48(8), O2 − V(1) − N2 117.45(9), O3 − V1 − N2 131.41(10).



Figure S3. Stacking of the vanadium complex molecules in **3**.MeCN. The overlapping regions of molecules involve centrosymmetrically-related units of the quinolinyl-benzimidazole groups.



Figure S4. ¹³C NMR spectrum of polyethylene from run 3.



Figure S5. ¹³C NMR spectrum of polyethylene from run 8.



Figure S6. ¹³C NMR spectrum of polyethylene from run 10.



Figure S7. Ethylene uptake for **3** in the presence of DMAC at different temperatures.



Figure S8. Ethylene uptake for **4** in the presence of DMAC at different temperatures.



Figure S9. Ethylene uptake for **5** in the presence of DMAC at different temperatures.



Figure S10. Ethylene uptake for **3** in the presence of DEAC at different temperatures.



Figure S11. Ethylene uptake for 4 in the presence of DEAC at different temperatures.



Figure S12. Ethylene uptake for **5** in the presence of DEAC at different temperatures.



Figure S13. PDIs for **3** at 50 and 80 °C.



Figure S14. PDIs for 4 at 50 °C.



Figure S15. PDIs for **5** at 50 and 80 °C.







Figure S17. MALDI-TOF of PCL sample initiated by 2 at 60 °C.



Figure S18. MALDI-TOF of PCL sample initiated by 6 in THF at 60 °C.



Figure S9. MALDI-TOF of PCL sample initiated by 7 in THF at 60 °C.



Figure S20. ¹H NMR spectrum of PCL sample (from run 3).



Figure S21. ¹³C NMR spectrum of PCL sample (from run 3).