Supplementary Information

for

Trifluoromethoxy-substituted nickel catalysts for producing highly branched

polyethylenes: impact of solvent, activator and *N*,*N'*-ligand on polymer properties

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| | Table of Contents | Page |
|----|--|-------------|
| 1. | ¹³ C NMR spectra of the polyethylenes | S2 |
| 2. | ¹⁹ F NMR spectra of Ni1 – Ni6 | S5 |
| 3. | ¹ H NMR spectra of Ni1 - Ni5 | S 8 |
| 4. | Comparison of activity and M_w of the PE generated by Ni1 with structurally related nickel catalysts | S11 |
| 5. | References | S 11 |

1.¹³C NMR spectra of the polyethylenes



Figure S1 ¹³C NMR spectrum of PE-30_{MM/2µ/T} along with a segment of the assigned polymer backbone (run 4, Table 6); recorded in C₆D₄Cl₂ at 100 °C.



Figure S2 ¹³C NMR spectrum of PE-30_{MM/2µ/H} along with a segment of the assigned polymer backbone (run 11, Table 7); recorded in C₆D₄Cl₂ at 100 °C.



Figure S3 ¹³C NMR spectrum of PE-30_{MM/1µ/H} along with a segment of the assigned polymer backbone (run 12, Table 7); recorded in C₆D₄Cl₂ at 100 °C.



Figure S4 ¹³C NMR spectrum of PE-70_{MM/2µ/T} along with a segment of the assigned polymer backbone (run 11, Table 6); recorded in C₆D₄Cl₂ at 100 °C.



Figure S5 ¹³C NMR spectrum of PE-30_{E/2µ/T} along with a segment of the assigned polymer backbone (run 3, Table 9); recorded in C₆D₄Cl₂ at 100 °C.



Figure S6 ¹³C NMR spectrum of PE-30_{E/2 μ /H} along with a segment of the assigned polymer backbone (run 11, Table 10); recorded in C₆D₄Cl₂ at 100 °C.



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Figure S7 ¹³C NMR spectrum of PE-30_{MM/1µ/H} along with a segment of the assigned polymer backbone (run 12, Table 10); recorded in C₆D₄Cl₂ at 100 °C.

2.19F NMR spectra of Ni1 – Ni6



Figure S8 ¹⁹F NMR spectrum of Ni1 in CDCl₃ at room temperature.



Figure S10 ¹⁹F NMR spectrum of Ni3 in CDCl₃ at room temperature.



Figure S12 ¹⁹F NMR spectrum of Ni5 in CDCl₃ at room temperature.



Figure S13 ¹⁹F NMR spectrum of Ni6 in CDCl₃ at room temperature.

3. ¹H NMR spectra of Ni1 - Ni5



Figure S14 ¹H NMR spectrum of Ni1 in CDCl₃ at room temperature.



Figure S15 ¹H NMR spectrum of Ni2 in CDCl₃ at room temperature.



Figure S16 ¹H NMR spectrum of Ni3 in CDCl₃ at room temperature.



Figure S17 ¹H NMR spectrum of Ni4 in CDCl₃ at room temperature.



Figure S18 ¹H NMR spectrum of Ni5 in CDCl₃ at room temperature.

4. Comparison of activity and M_w of the PE generated by Ni1 with structurally related nickel catalysts



Figure S19 Comparison of activity and M_w of the polyethylene generated by Ni1 (R = OCF₃) with precatalyst **B** (Chart 1, R = *t*-Bu,¹ CHPh₂,² OMe³); all precatalysts were screened using MAO and under comparable conditions, 30 °C, P_{C2H4} = 10 atm, solvent = toluene

5. References

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