

Electronic Supplementary Information for

Synthesis and Structural Characterization of Zirconium Complexes Supported by Tridentate Pyrrolide-Imino Ligands with pendant *N*-, *O*- and *S*-donor groups and Their Application in Ethylene Polymerization

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Table S1 Crystal data and structure refinement for **3b**.

Molecular formula	C ₄₁ H ₃₄ Cl ₂ N ₄ O ₂ Zr
Formula weight (g mol ⁻¹)	776.84
T (K)	150(2)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	9.5518(2)
<i>b</i> (Å)	23.0867(6)
<i>c</i> (Å)	16.3796(5)
α (°)	90
β (°)	104.2780(10)
γ (°)	90
V (Å ³)	3500.45(16)
<i>Z</i>	4
ρ_{calcd} (g cm ⁻³)	1.474
μ (mm ⁻¹)	0.510
<i>F</i> (000)	1592
Crystal size (mm)	0.38 x 0.13 x 0.12
θ range (°)	2.94 to 27.48
Limiting indices (<i>h</i> , <i>k</i> , <i>l</i>)	$-12 \leq h \leq 12$ $-29 \leq k \leq 29$ $-21 \leq l \leq 21$
Reflections collected	31533
Reflections unique (<i>R</i> _{int})	7995 (0.0513)
Completeness to θ_{max} (%)	99.7
Data / restraints / param.	7995 / 0 / 452
Min. and max. transmission	0.941 and 0.890
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0361
w <i>R</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0751
<i>R</i> ₁ (all data)	0.0495
w <i>R</i> ₂ (all data)	0.0804
Largest diff. peak and hole (e Å ⁻³)	0.349 and -0.476

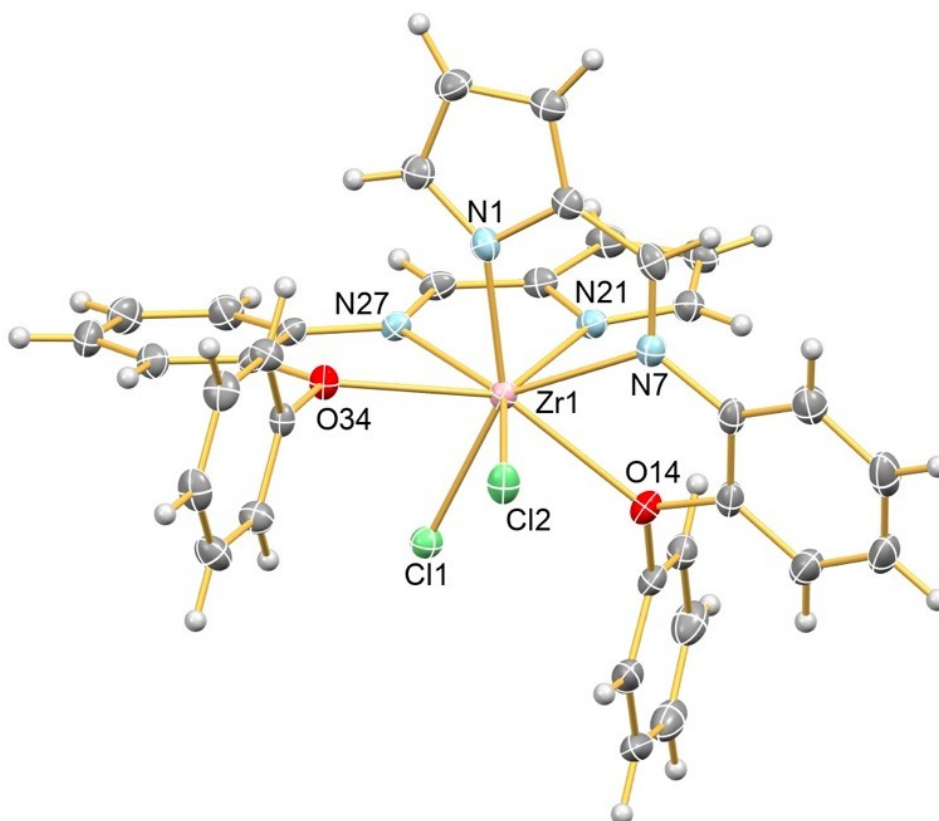


Figure S1. ORTEP drawing of $[\text{Zr}\{2\text{-(C}_4\text{H}_3\text{N-2-CH=N)C}_2\text{H}_4\text{NHPh}\}(\text{THF})\text{Cl}_3]$ (**3b**) (thermal ellipsoids drawn at the 30% probability level). Selected bond distances (Å) and angles (deg): Zr(1)-N(1) = 2.2169(18), Zr(1)-N(7) = 2.3436(18), Zr(1)-N(21) = 2.2356(17), Zr(1)-N(27) = 2.3461(17), Zr(1)-O(14) = 2.4932(15), Zr(1)-O(34) = 2.5347(14), Zr(1)-Cl(1) = 2.4834(6), Zr(1)-Cl(2) = 2.4729(5), N(1)-Zr(1)-N(21) = 86.75(6), N(1)-Zr(1)-N(7) = 71.56(6), N(21)-Zr(1)-N(7) = 76.15(6), N(1)-Zr(1)-N(27) = 80.06(6), N(21)-Zr(1)-N(27) = 70.68(6), N(7)-Zr(1)-N(27) = 137.13(6), N(1)-Zr(1)-Cl(2) = 96.32(5), N(21)-Zr(1)-Cl(2) = 147.54(5), N(7)-Zr(1)-Cl(2) = 74.28(4), N(27)-Zr(1)-Cl(2) = 141.73(4), N(1)-Zr(1)-Cl(1) = 148.41(5), N(21)-Zr(1)-Cl(1) = 105.41(5), N(7)-Zr(1)-Cl(1) = 139.21(5), N(27)-Zr(1)-Cl(1) = 76.91(4), Cl(2)-Zr(1)-Cl(1) = 88.704(19), N(1)-Zr(1)-O(14) = 135.37(6), N(21)-Zr(1)-O(14) = 74.20(6), N(7)-Zr(1)-O(14) = 64.89(6), N(27)-Zr(1)-O(14) = 127.42(5), Cl(2)-Zr(1)-O(14) = 81.32(4), Cl(1)-Zr(1)-O(14) = 76.20(4), N(1)-Zr(1)-O(34) = 73.99(6), N(21)-Zr(1)-O(34) = 133.43(6), N(7)-Zr(1)-O(34) = 132.24(5), N(27)-Zr(1)-O(34) = 64.52(5), Cl(2)-Zr(1)-O(34) = 77.78(3), Cl(1)-Zr(1)-O(34) = 76.70(4), O(14)-Zr(1)-O(34) = 145.91(5).

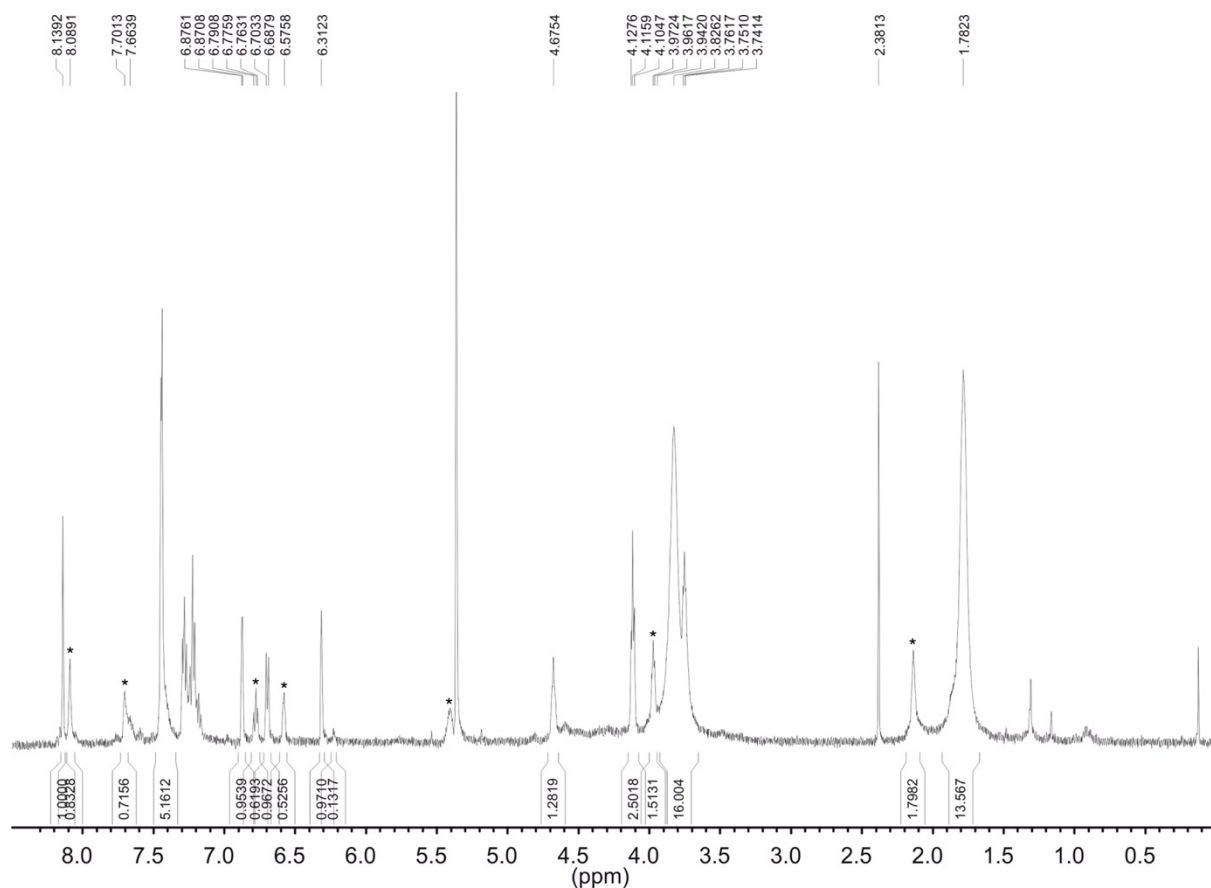


Figure S2. ^1H NMR spectrum of **2a** (500 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$). (* refers to the presence of unidentified product(s) that arise from the decomposition of **2a** in solution).

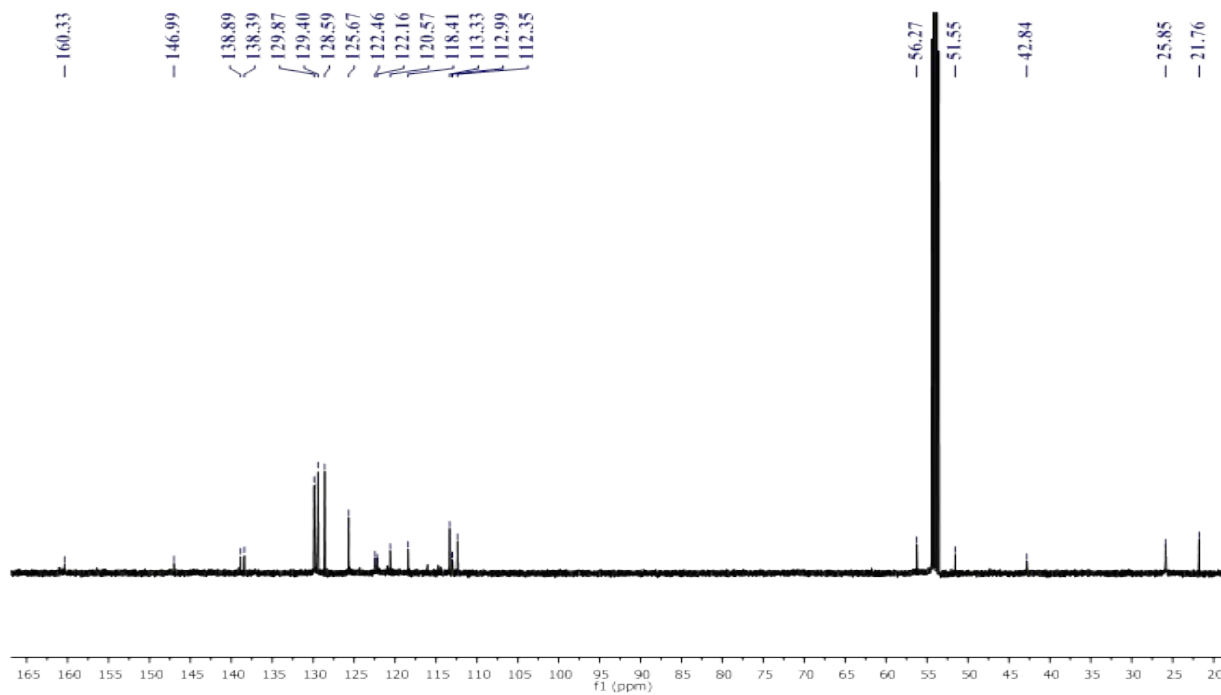


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2a** (125 MHz, CD_2Cl_2 , 25 °C).

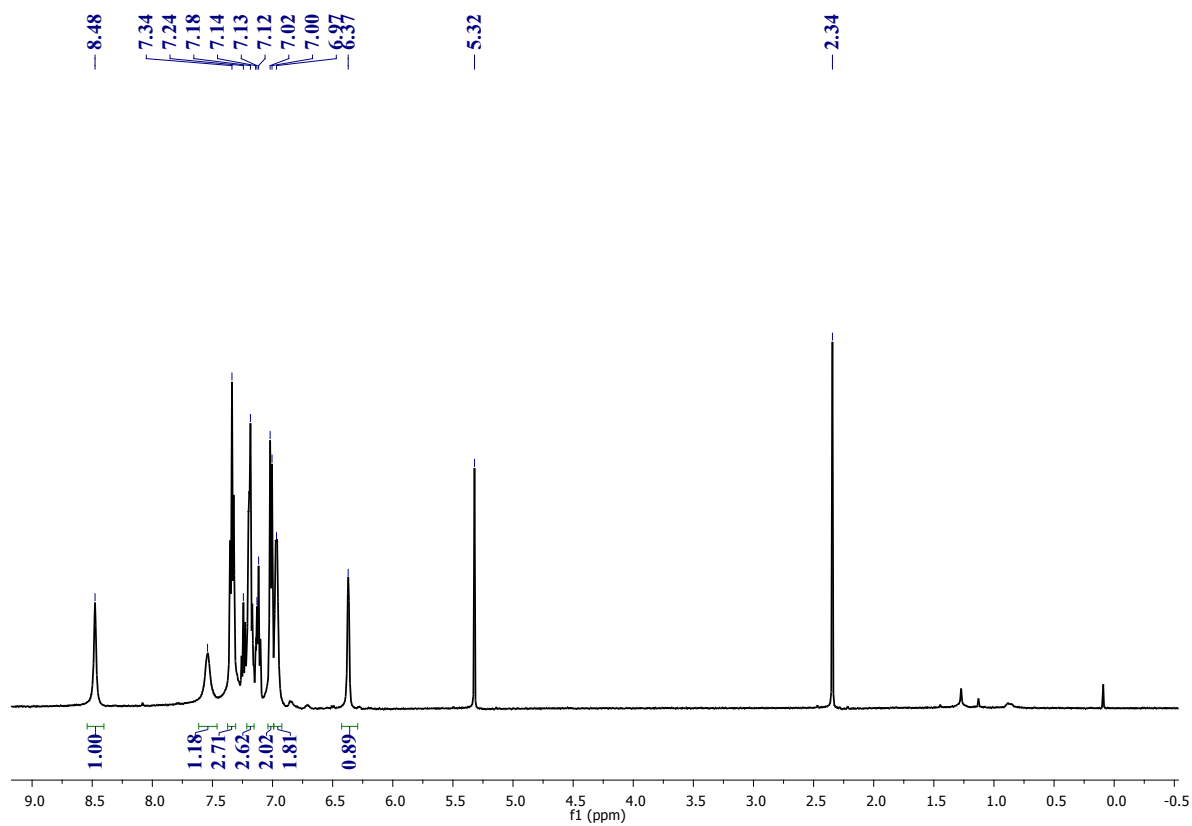


Figure S4. ^1H NMR spectrum of **2b** (500 MHz, CD_2Cl_2 , 25 °C)

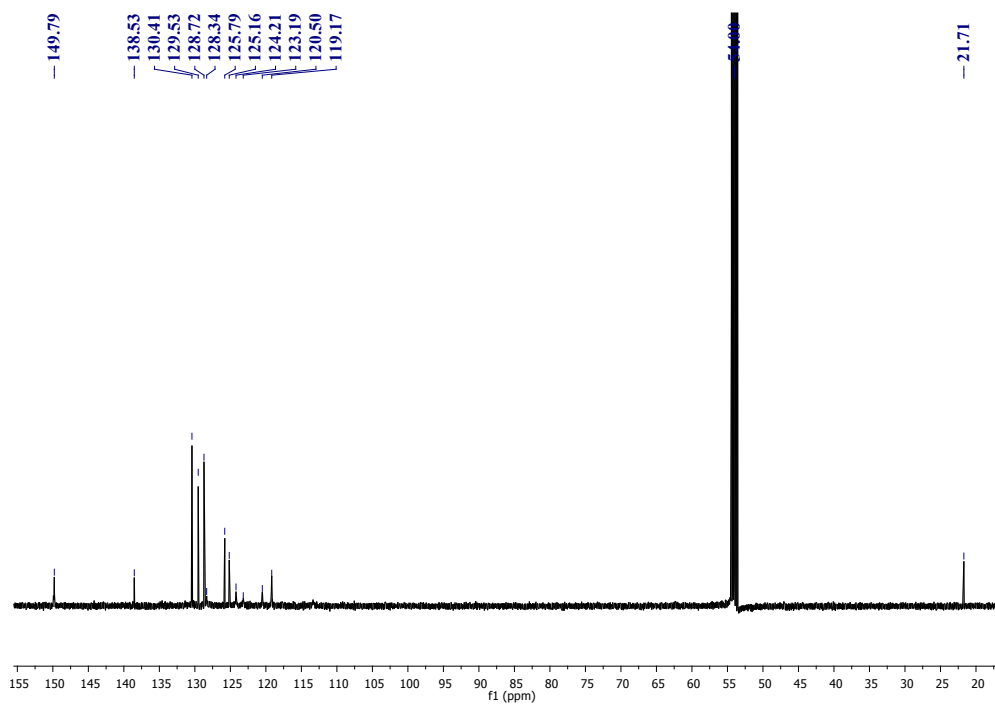


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2b** (125 MHz, CD_2Cl_2 , 25 °C)

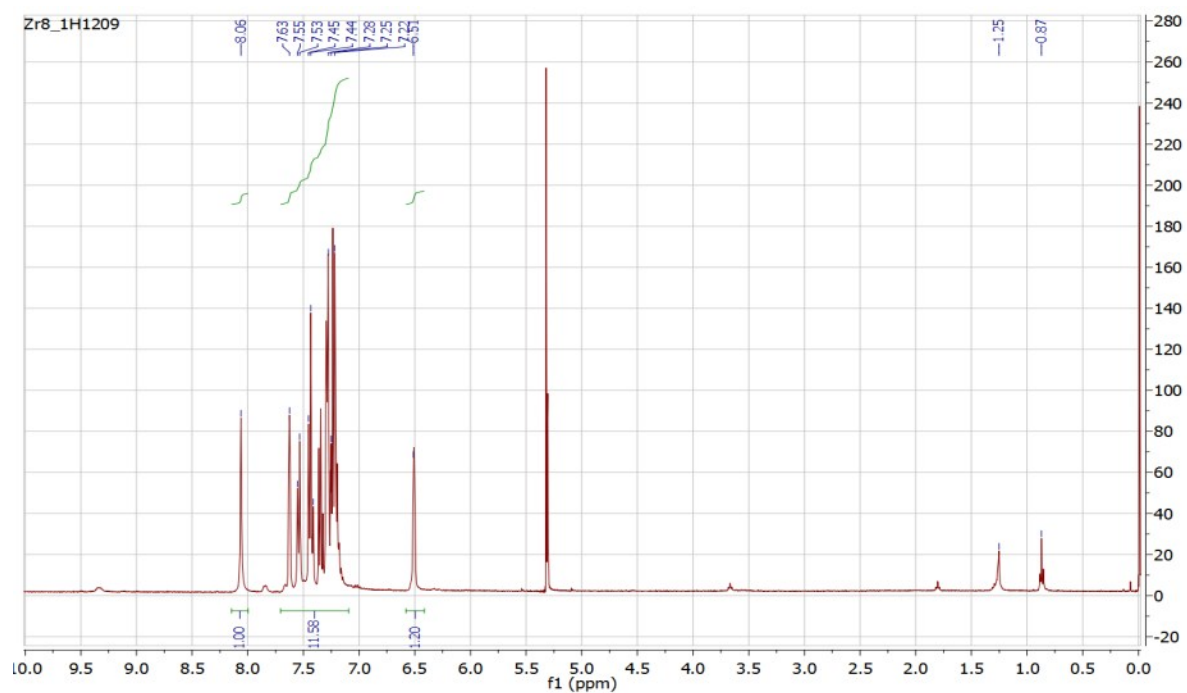


Figure S6. ^1H NMR spectrum of **2c** (400 MHz, CD_2Cl_2 , 25 °C)

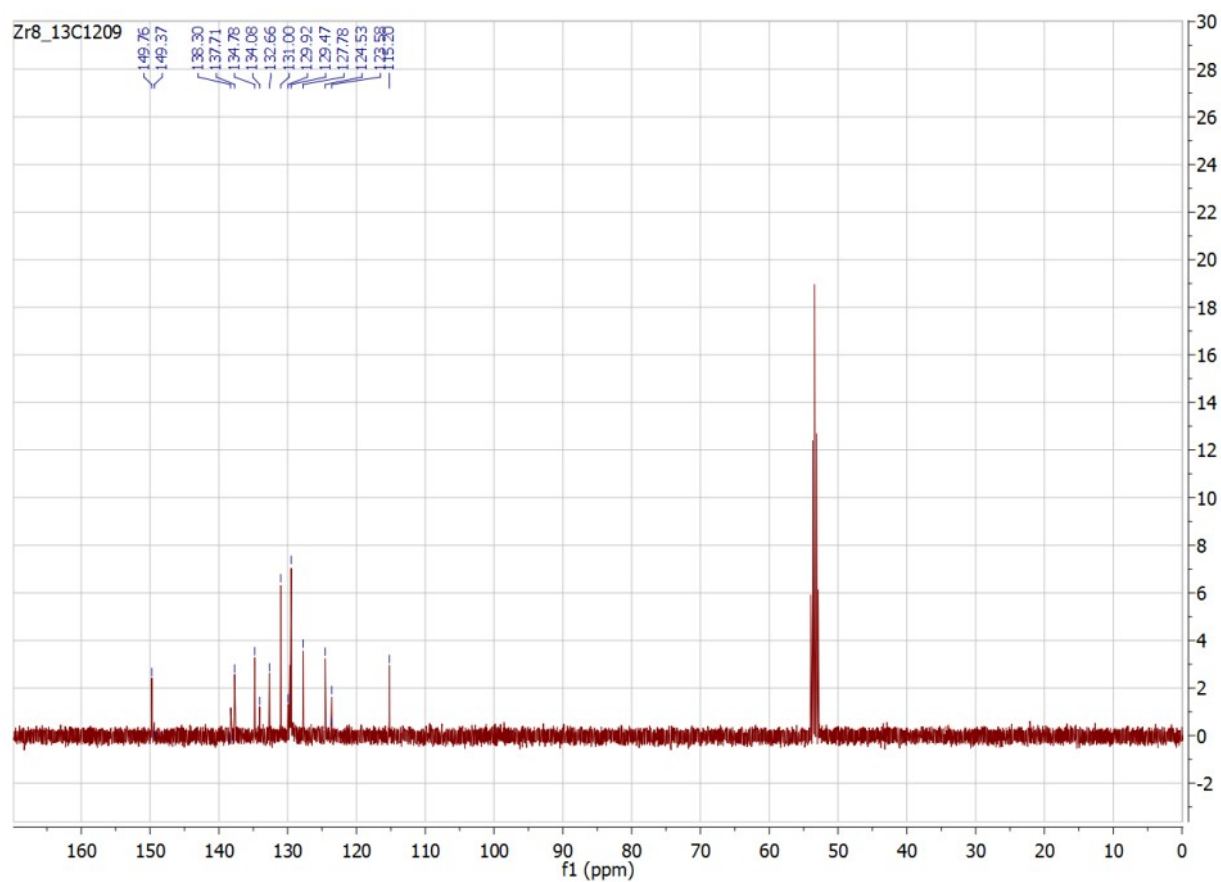


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2c** (100 MHz, CD_2Cl_2 , 25 °C)

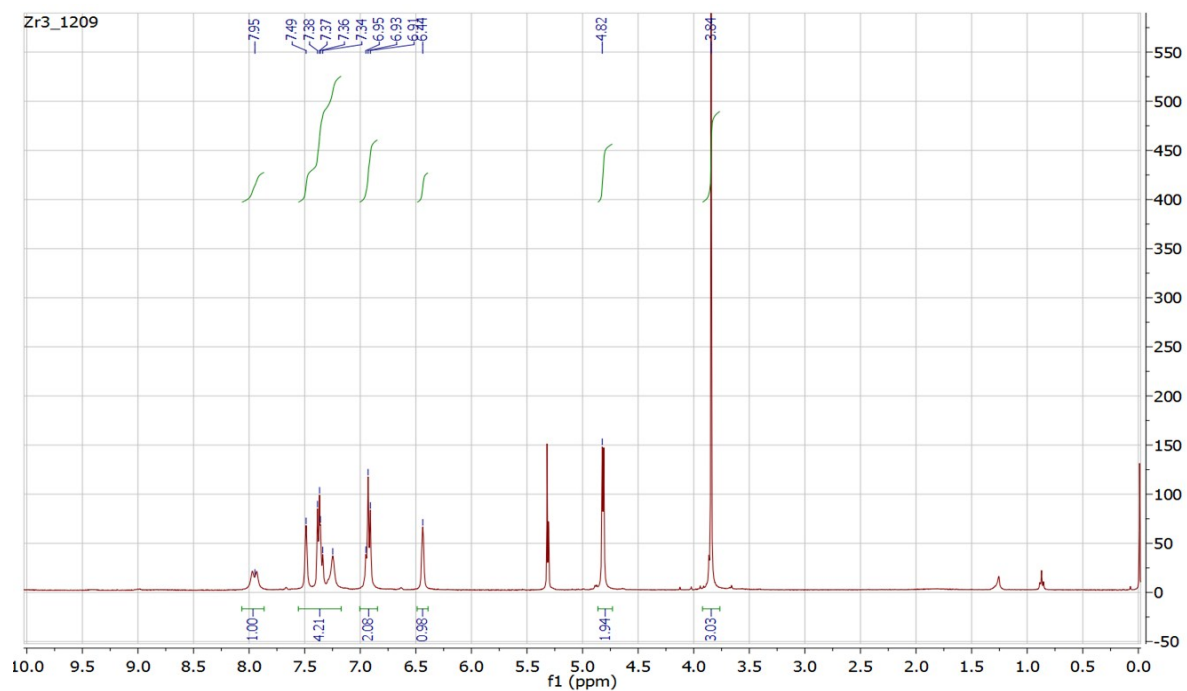


Figure S8. ^1H NMR spectrum of **2d** (400 MHz, CD_2Cl_2 , 25 °C)

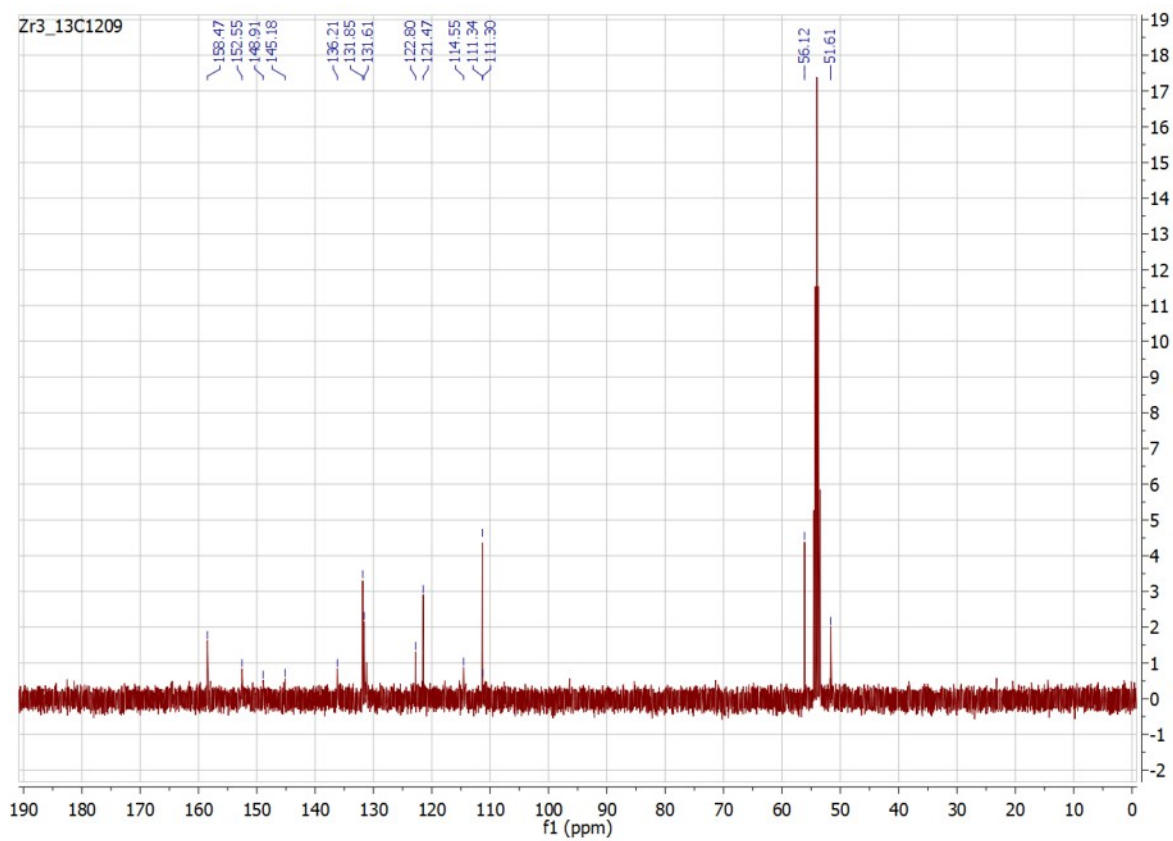


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2d** (100 MHz, CD_2Cl_2 , 25 °C)

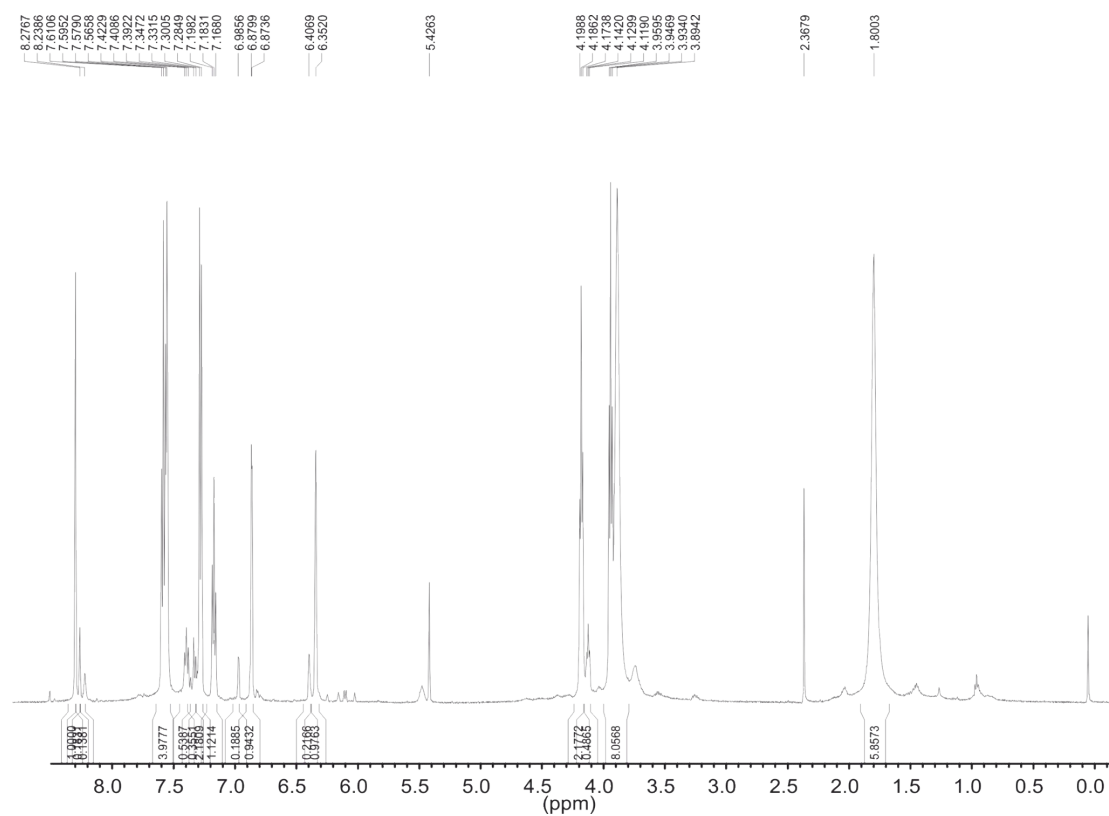


Figure S10. ^1H NMR spectrum of **4a** (500 MHz, CD_2Cl_2 , 25 °C)

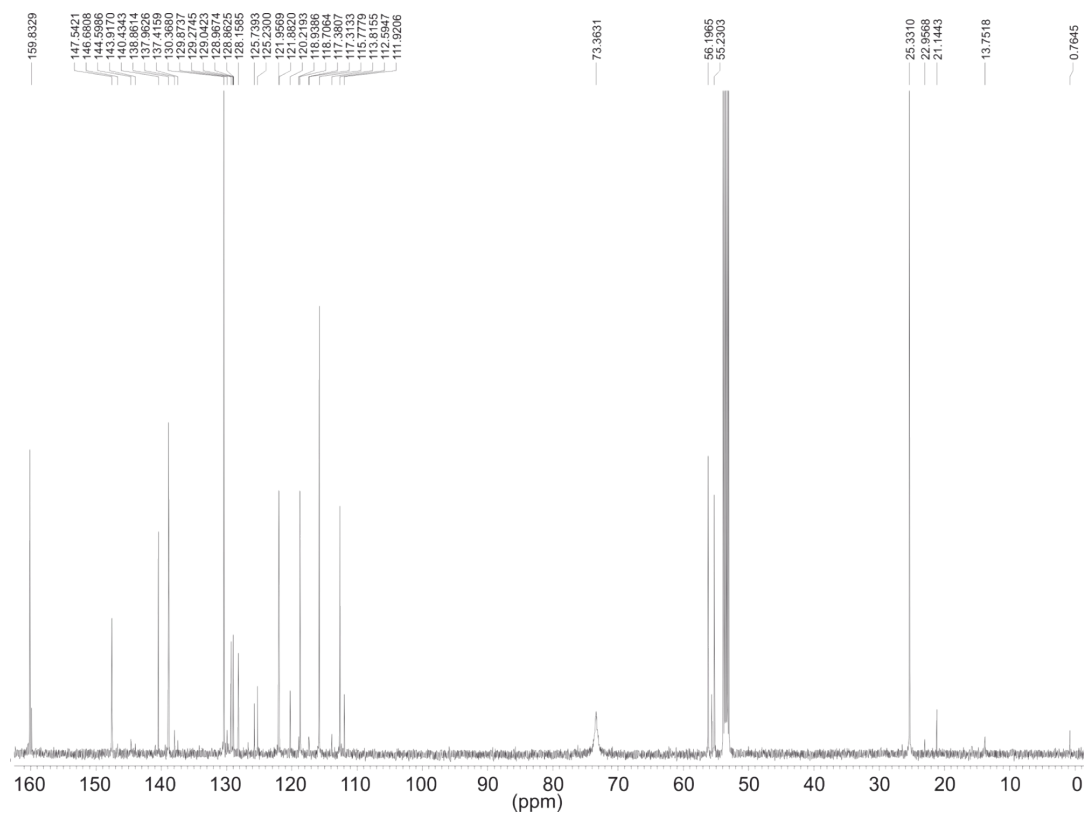


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4a** (125 MHz, CD_2Cl_2 , 25 °C)

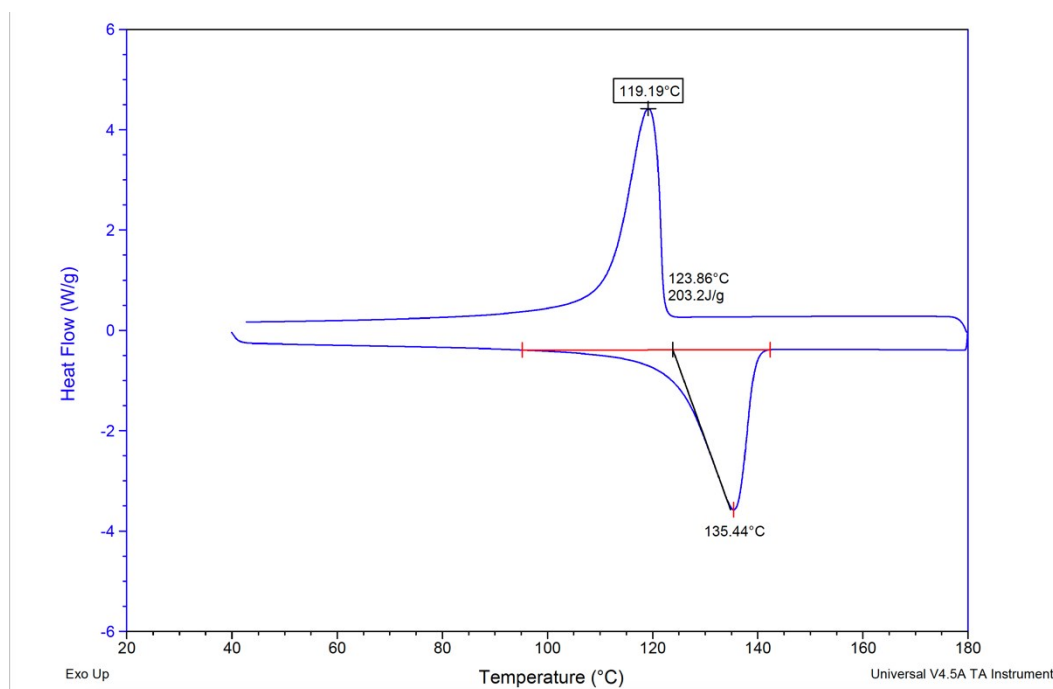


Figure S12. DSC trace of polyethylene produced by **2a**/MAO system (60 °C, 5 bar, time = 15 min, [Al/Zr] = 500).

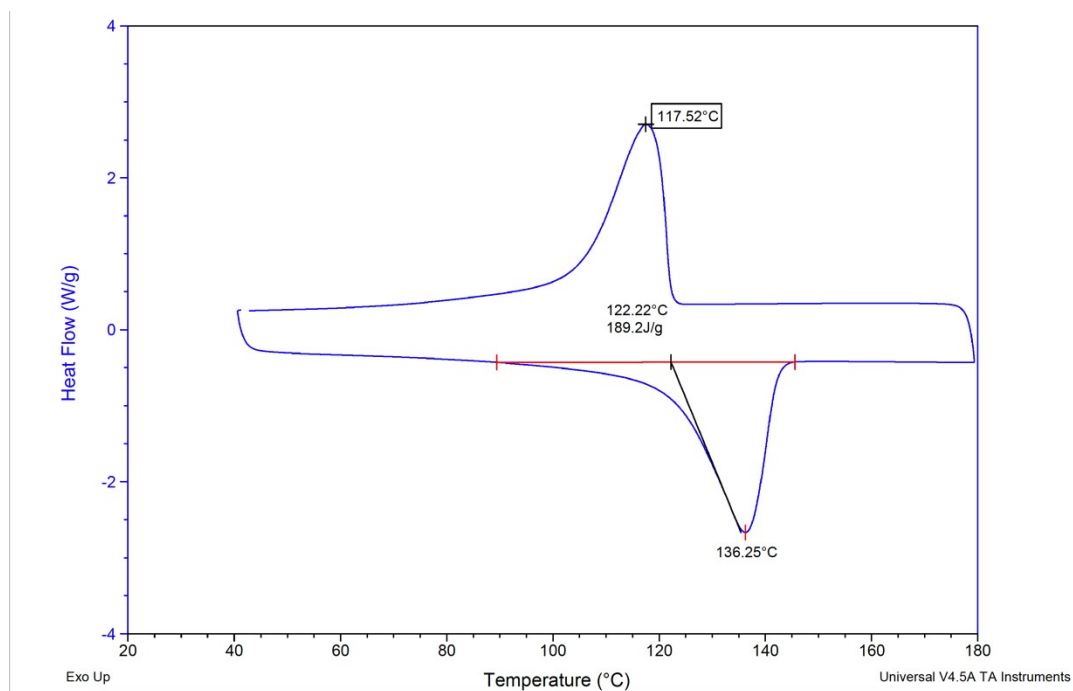


Figure S13. DSC trace of polyethylene produced by **2b**/MAO system (60 °C, 5 bar, time = 15 min, [Al/Zr] = 500).

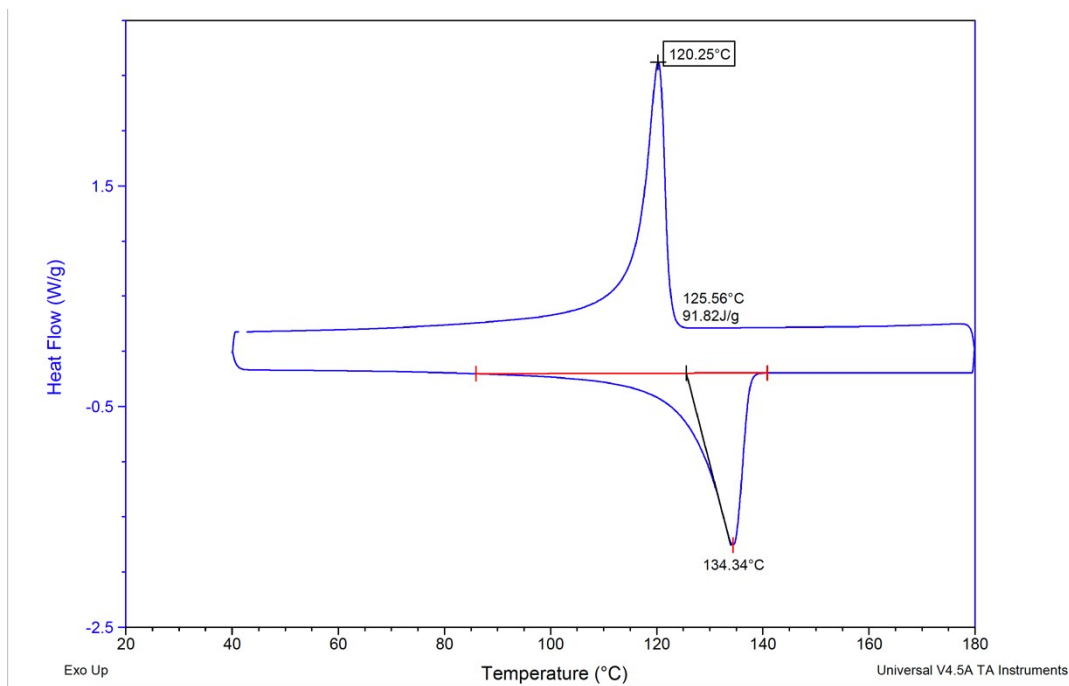


Figure S14. DSC trace of polyethylene produced by **2c**/MAO system (60 °C, 5 bar, time = 15 min, [Al/Zr] = 500).

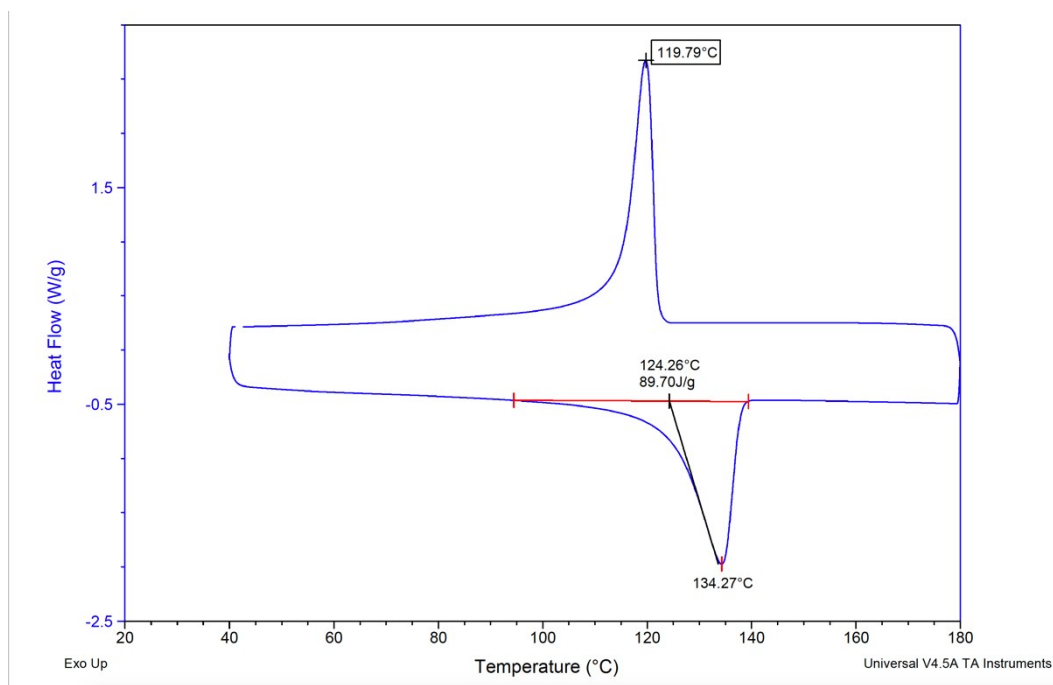


Figure S15. DSC trace of polyethylene produced by **2d**/MAO system (60 °C, 5 bar, time = 15 min, [Al/Zr] = 500).

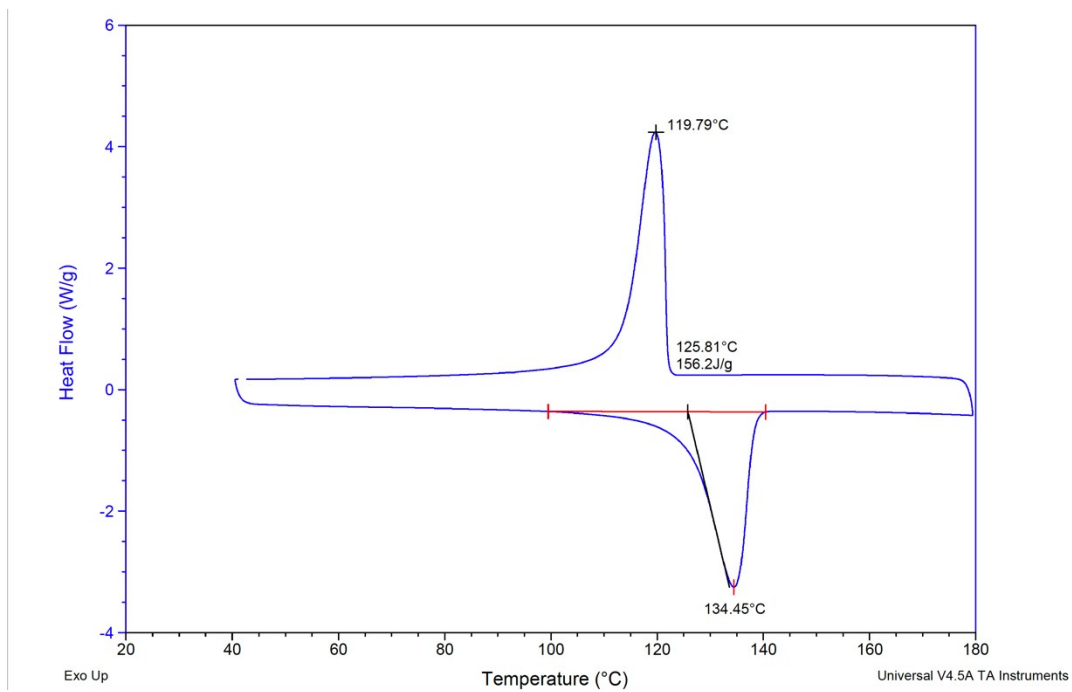


Figure S16. DSC trace of polyethylene produced by **4a**/MAO system (60 °C, 5 bar, time = 15 min, [Al/Zr] = 500).