Electronic Supplementary Information (ESI)

for

Synthesis of Ultrahigh Molecular Weight Polymers by Homopolymerisation of Higher α-Olefins Catalysed by Aryloxo-Modified Half-Titanocenes

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2 Additional data for polymerisation of 1-octene (OC) using $Cp^*TiMe_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**4**) – Al^iBu_3 – $[Ph_3C][B(C_6F_5)_4]$ catalyst.

3. Selected NMR spectra of poly(α-olefin)s.

4. Selected DSC thermograms.

1. Additional data for polymerisation of 1-decene (DC), 1-dodecene (DD) using Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (1) -MAO catalyst: Effect of Al/Ti molar ratio.

Table S1. Polymerisation of 1-decene (DC), 1-dodecene (DD) using Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**) -MAO catalyst: Effect of Al/Ti molar ratio.[a]

run	α-olefin	Al/Ti	yield/ mg	TON[b]	activity[c]	M_n[d]×10^{-4}	M_w/M_n[d]
3	DC	2000	922	6570	1840	57.4	1.84
4	DC	2000	904	6450	1810	43.5	1.78
S1	DC	3000	1011	7210	2020	68.9	1.32
S2	DC	3000	1016	7240	2030	67.6	1.40
S3	DC	4000	1270	9050	2540	67.5	1.30
S4	DC	6000	1104	7870	2210	78.8	1.23
S5	DC	6000	1167	8320	2334	73.0	1.25
5	DD	2000	694	4120	1390	52.5	1.35
S6	DD	3000	606	3600	1210	57.8	1.58
S7	DD	4000	683	4060	1370	65.3	1.38
S8	DD	4000	652	3870	1300	62.8	1.43
S9	DD	6000	626	3720	1250	60.4	1.54

[a]Conditions: complex 1.0 μmol, α-olefin 5.0 mL, d-MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO), 25 °C, 30 min; [b]TON (turnover number) = (mmol of α-olefin reacted)/(mmol-Ti); [c]Activity = kg-polymer/mol-Ti·h; [d]GPC data in THF *vs* polystyrene standards.

2 Additional data for polymerisation of 1-octene (OC) using Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (4) – Al^{i}Bu$_3$ – [Ph$_3$C][B(C$_6$F$_5$)$_4$] catalyst.

Table S2. Polymerisation of 1-octene (OC) using Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**4**) – Al^{i}Bu$_3$ – [Ph$_3$C][B(C$_6$F$_5$)$_4$] catalyst.[a]

run	α-olefin	Time	yield/ mg	TON[b]	activity[c]	M_n[d]×10^{-5}	M_w/M_n[d]
S10	OC	3	76.4	2720	6110	11.2	1.39
22	OC	3	70.2	2500	5620	11.8	1.54
23	OC	5	125.4	4470	6020	15.9	1.65
S11	OC	7	151.7	5410	5200	19.4	1.39
S12	OC	10	163.7	5840	3930	18.7	1.69
24	OC	10	160.3	5710	3850	20.0	1.89
S13	OC	15	188.3	6710	3010	19.4	1.84
25	OC	20	198.7	7080	2380	19.7	2.04
S14	OC	30	252.4	9000	2020	21.2	2.01
26	OC	30	237.7	8470	1900	24.5	1.90

[a] Reaction conditions: olefins 5.0 mL, cat. 0.25 μmol, -30 ◦C, Ti/[Ph$_3$C][B(C$_6$F$_5$)$_4$]/Al^{i}Bu^3 = 1.0/3.0/500; [b]TON (turnover number) = (mmol of α-olefin reacted)/(mmol-Ti); [c]Activity = kg-polymer/mol-Ti·h; [d]GPC data in THF *vs* polystyrene standards.

3. Selected ^{13}C and ^{1}H NMR spectra of poly(α-olefin)s.

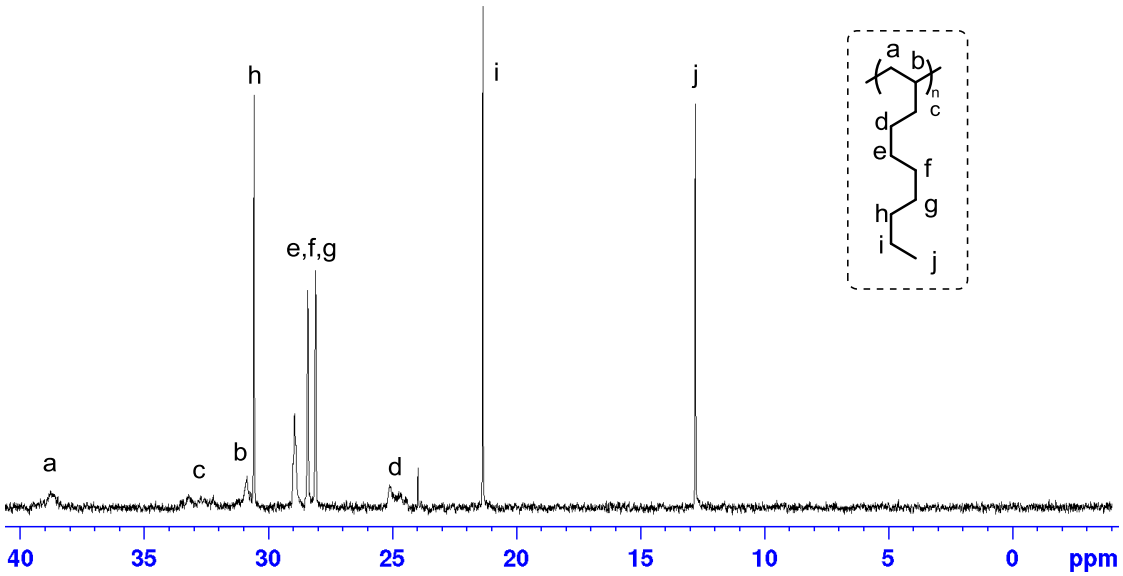

Figure S3-1. ^{13}C NMR spectrum in poly(1-decene) prepared by Cp*$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) - MAO catalyst (in $CDCl_3$ at 25 ºC, run 3, Table 1) .

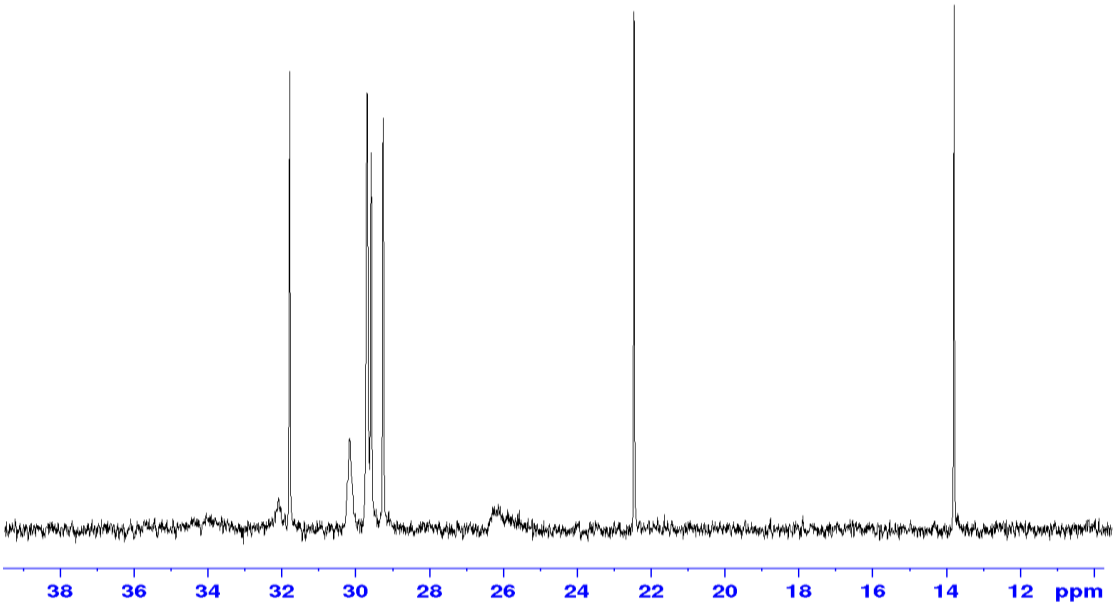

Figure S3-2. ^{13}C NMR spectrum in poly(1-octene) prepared by Cp*$TiMe_2$(O-2,6-$^{i}Pr_2C_6H_3$) **(4)** - borate catalyst (in $CDCl_3$ at 25 ºC, run 25, Table 2).

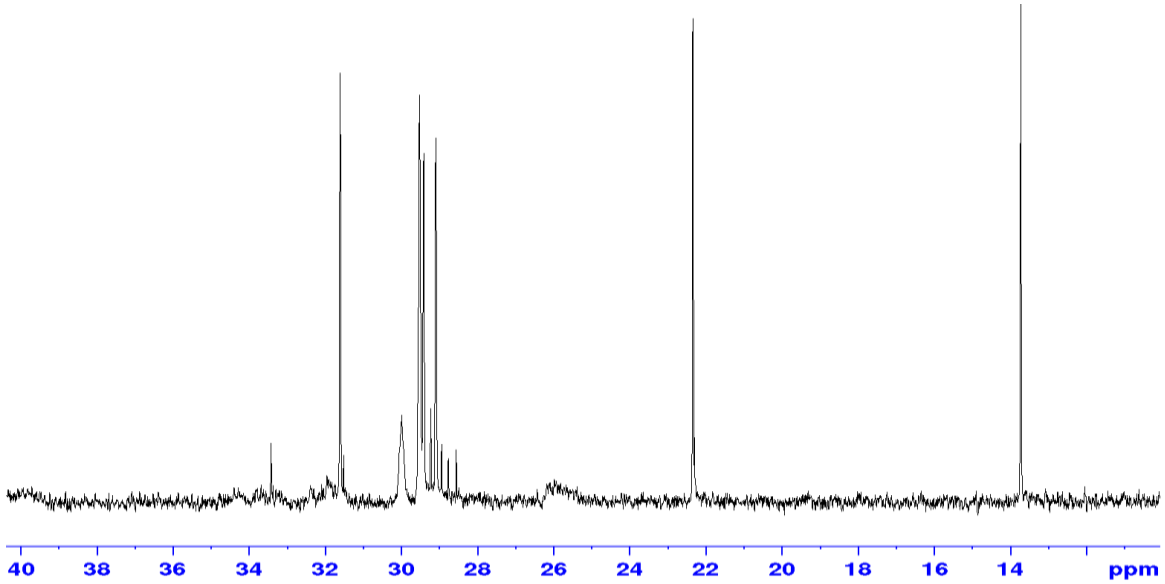

Figure S3-3. ^{13}C NMR spectrum in poly(1-dodecene) prepared by $Cp^*TiMe_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ **(4)** - borate catalyst (in $CDCl_3$ at 25 ºC, run 27, Table 2).

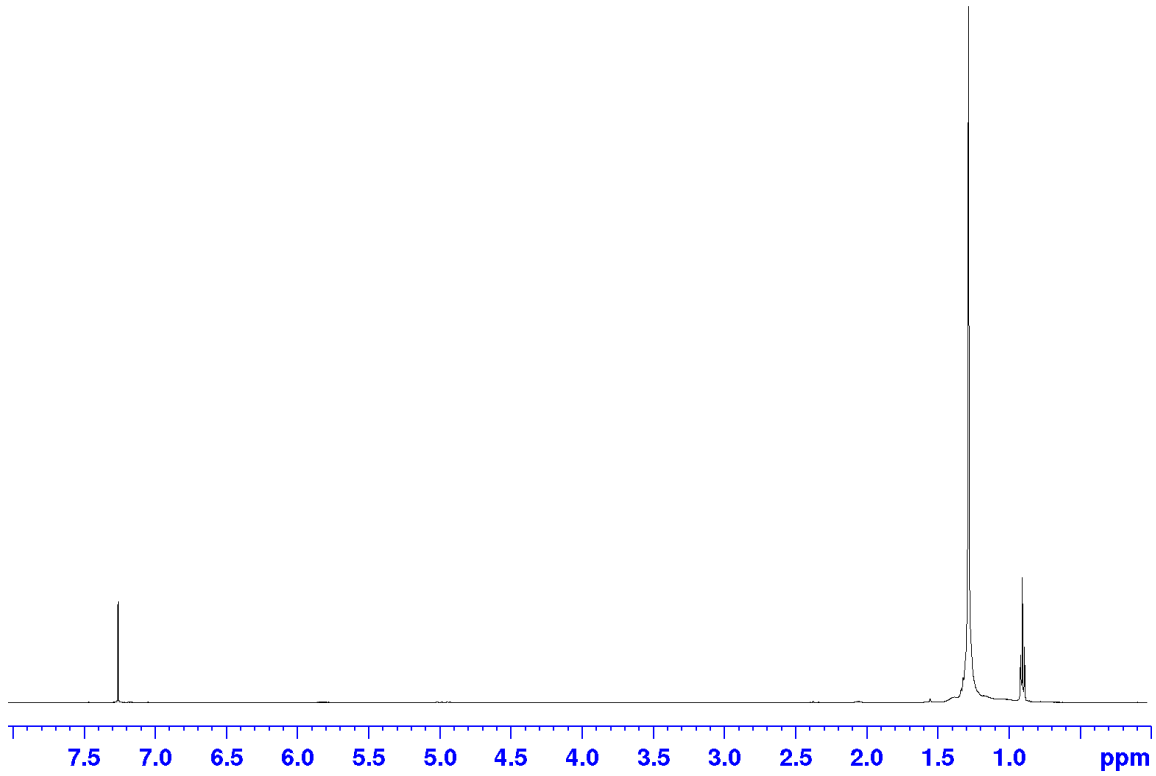

Figure S3-4. ^{1}H NMR spectrum in poly(1-hexadecene) prepared by $Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ - MAO catalyst (in $CDCl_3$ at 25 ºC, run 6, Table 1).

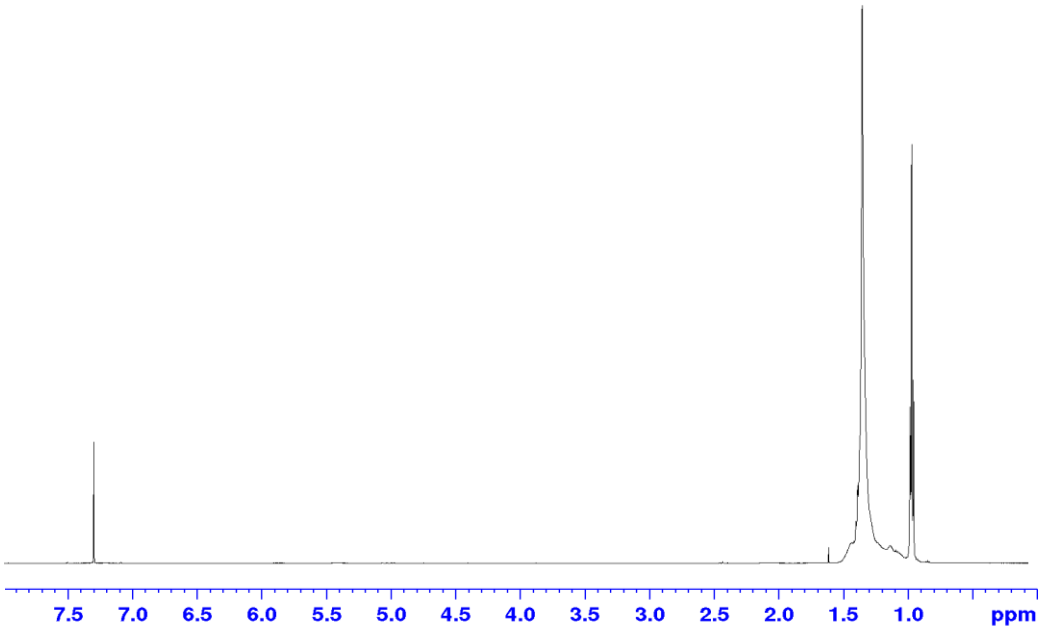

Figure S3-5. ^{1}H NMR spectrum in poly(1-decene) prepared by $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ **(2)** - MAO catalyst system. (in $CDCl_3$ at 25 ºC, run 10, Table 1).

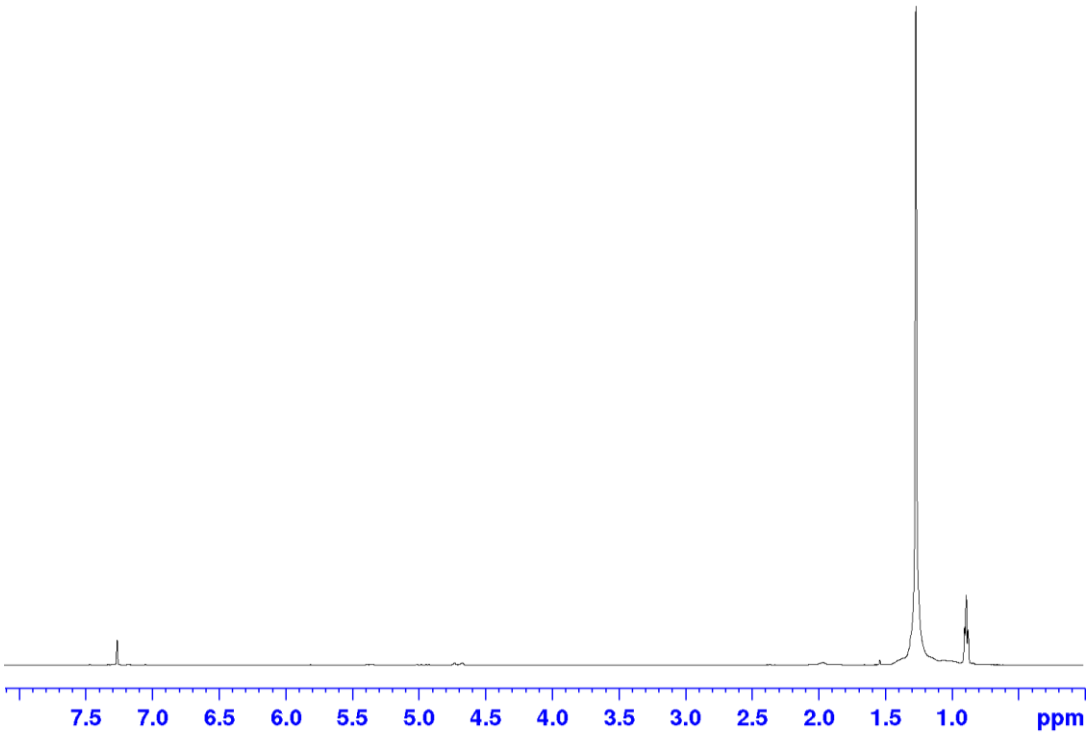

Figure S3-6. ^{1}H NMR spectrum in poly(1-hexadecene) prepared by $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ **(2)** - MAO catalyst (in $CDCl_3$ at 25 ºC, run 13, Table 1).

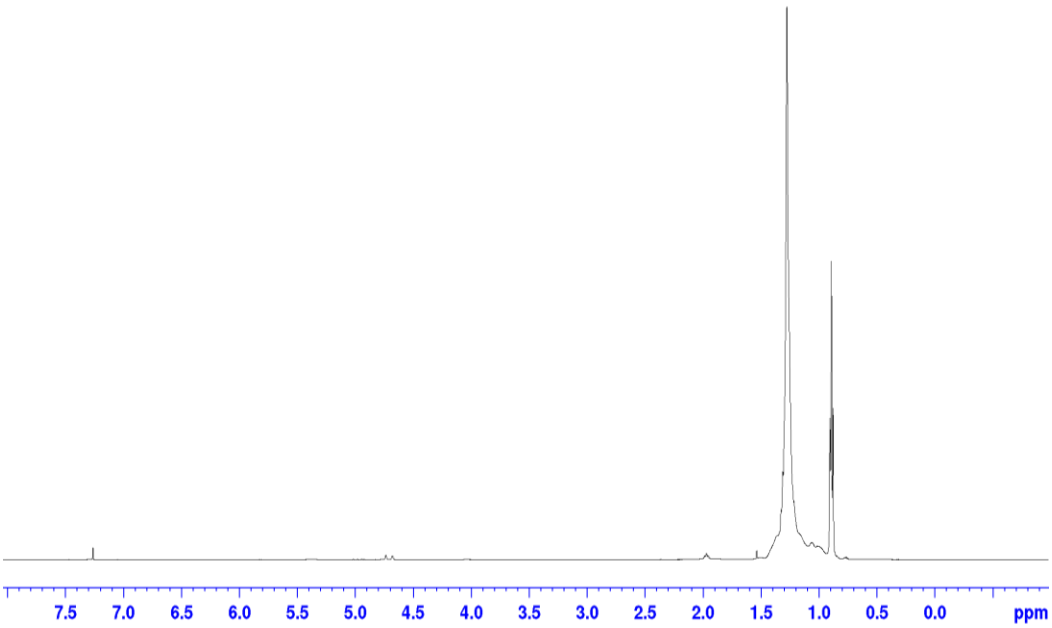

Figure S3-7. ^{1}H NMR spectrum in poly(1-decene) prepared by Cp_2ZrCl_2 **(3)** - MAO catalyst (in $CDCl_3$ at 25 ºC, run 17, Table 1).

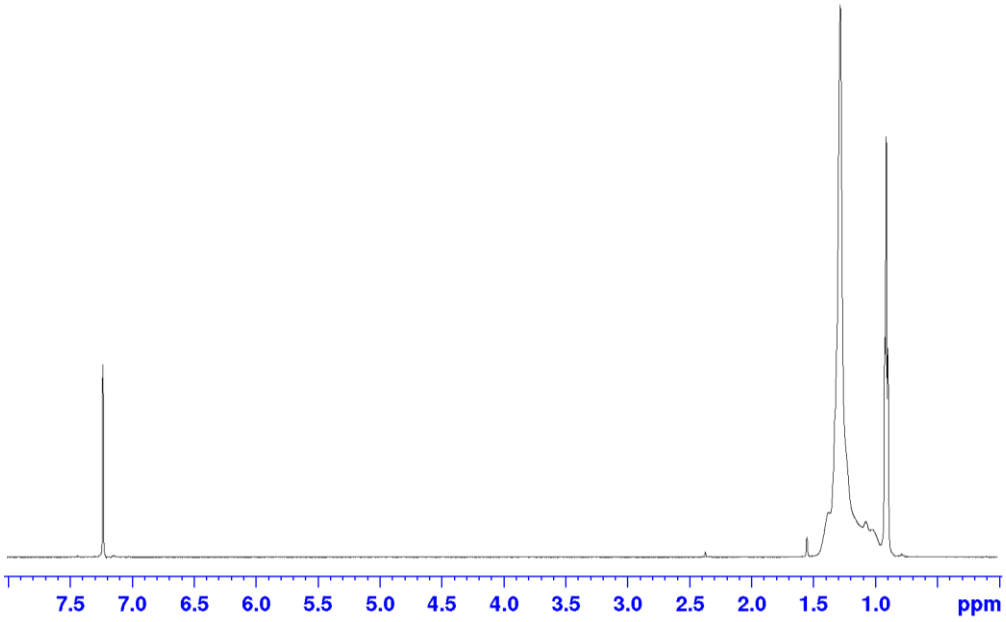

Figure S3-8. ^{1}H NMR spectrum in poly(1-octene) prepared by $Cp^*TiMe_2(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)$ **(4)** - borate catalyst system. (in $CDCl_3$ at 25 ºC, run 22, Table 2).

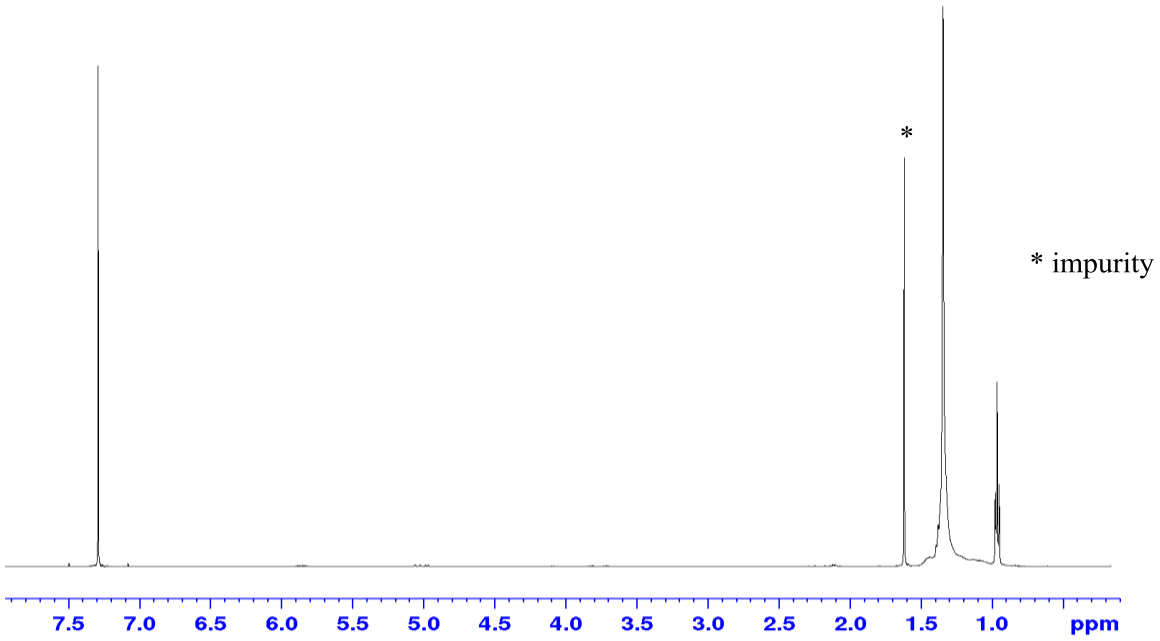

Figure S3-9. ^{1}H NMR spectrum in poly(1-octene) prepared by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) **(4)** - borate catalyst. (in $CDCl_3$ at 25 ºC, run 26, Table 2).

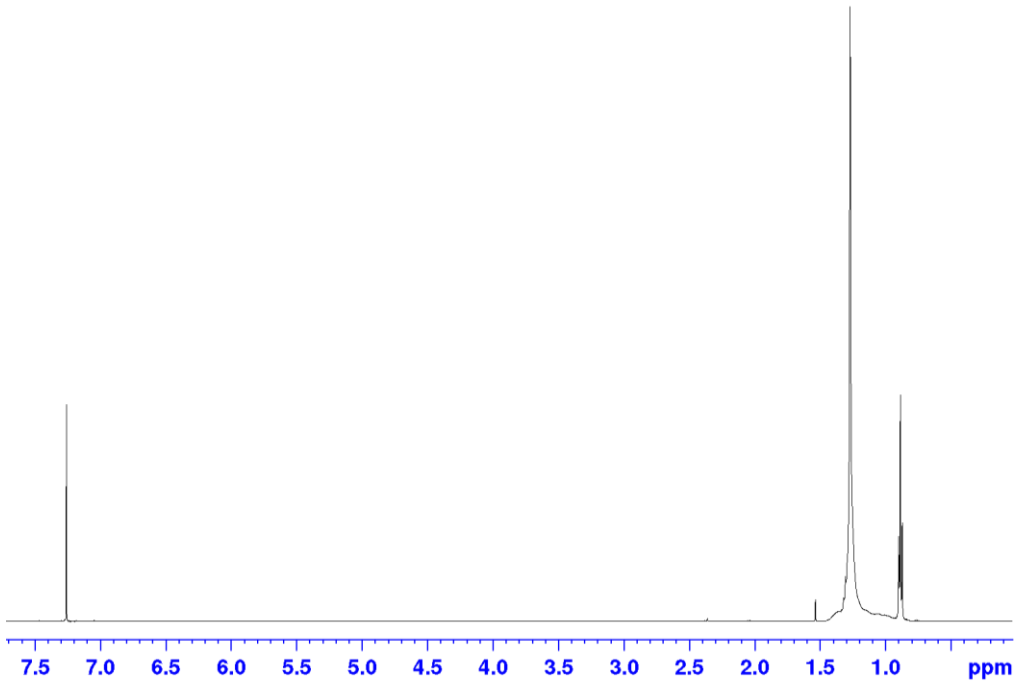

Figure S3-10. ^{1}H NMR spectrum in poly(1-dodecene) prepared by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) **(4)** - borate catalyst system. (in $CDCl_3$ at 25 ºC, run 27, Table 2).

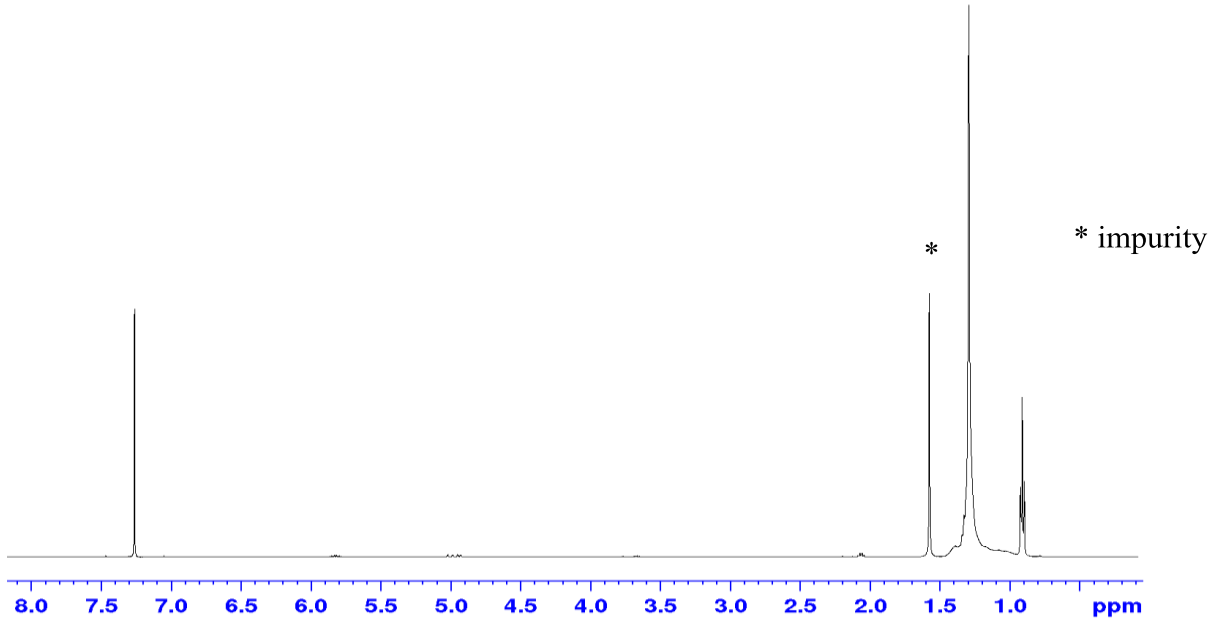

Figure S3-11. ^{1}H NMR spectrum in poly(1-dodecene) prepared by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) **(4)** - borate catalyst (in $CDCl_3$ at 25 ºC, run 28, Table 2).

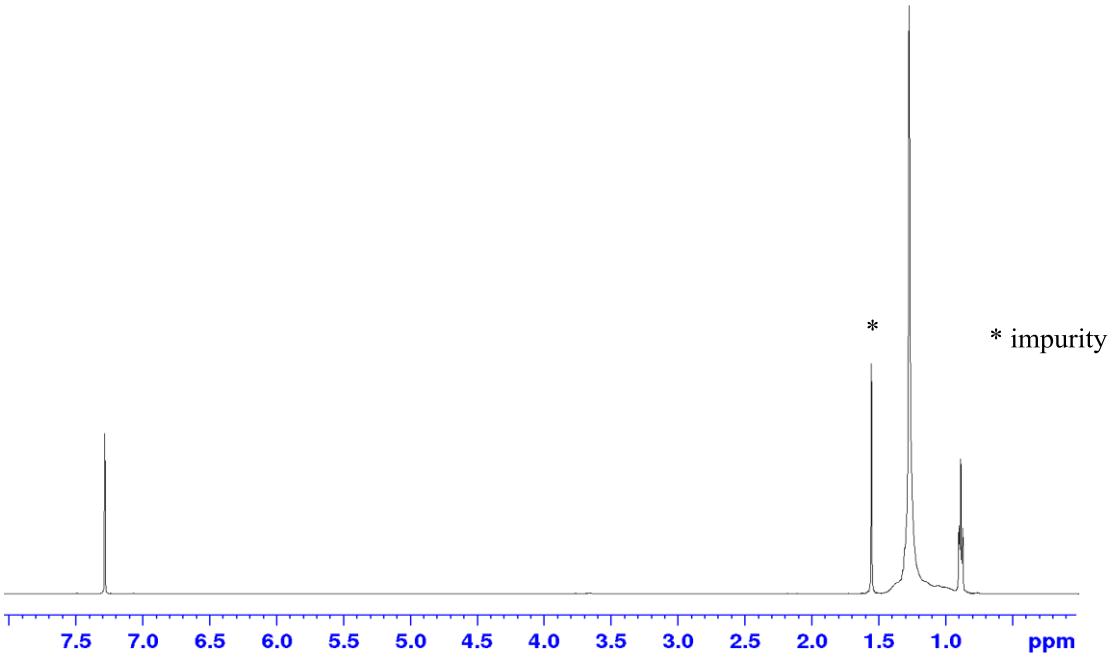

Figure S3-12. ^{1}H NMR spectrum in poly(1-octene) prepared by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) **(4)** - borate catalyst (in $CDCl_3$ at 25 ºC, run 29, Table 2).

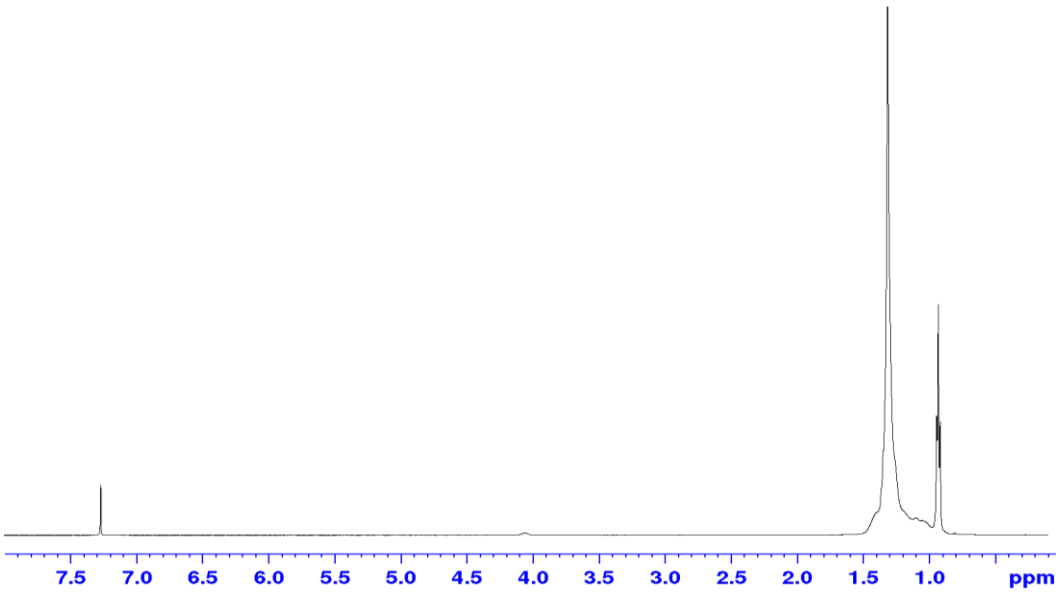

Figure S3-13. ^{1}H NMR spectrum in poly(1-decene) prepared by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) - MAO catalyst (in $CDCl_3$ at 25 ºC, run S3, Table S1).

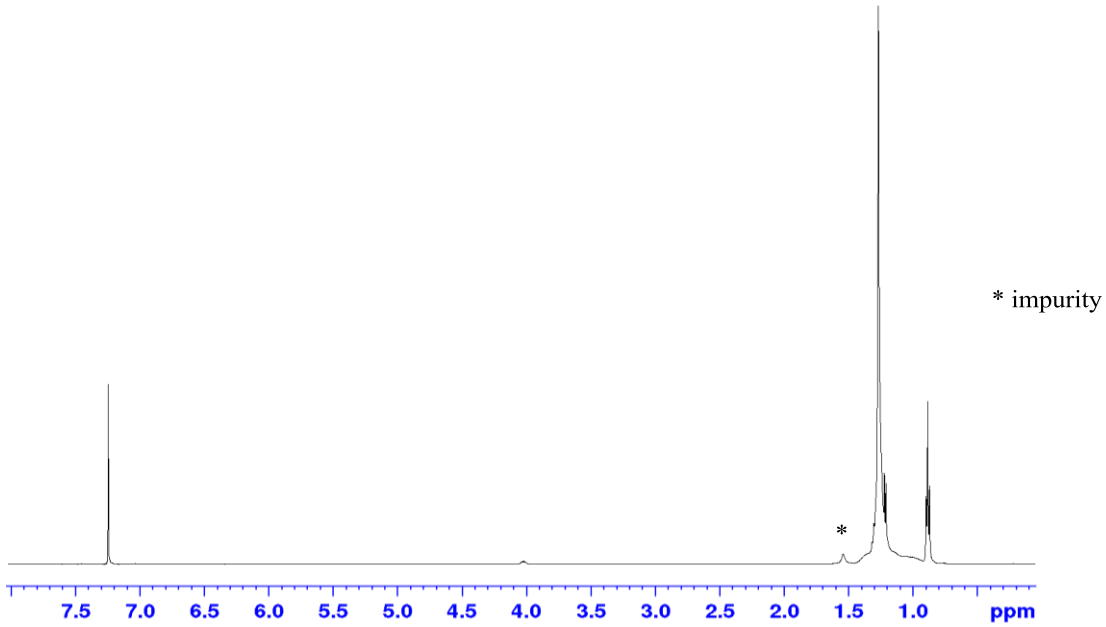

Figure S3-14. ^{1}H NMR spectrum in poly(1-decene) prepared by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) - MAO catalyst (in $CDCl_3$ at 25 ºC, run S4, Table S1).

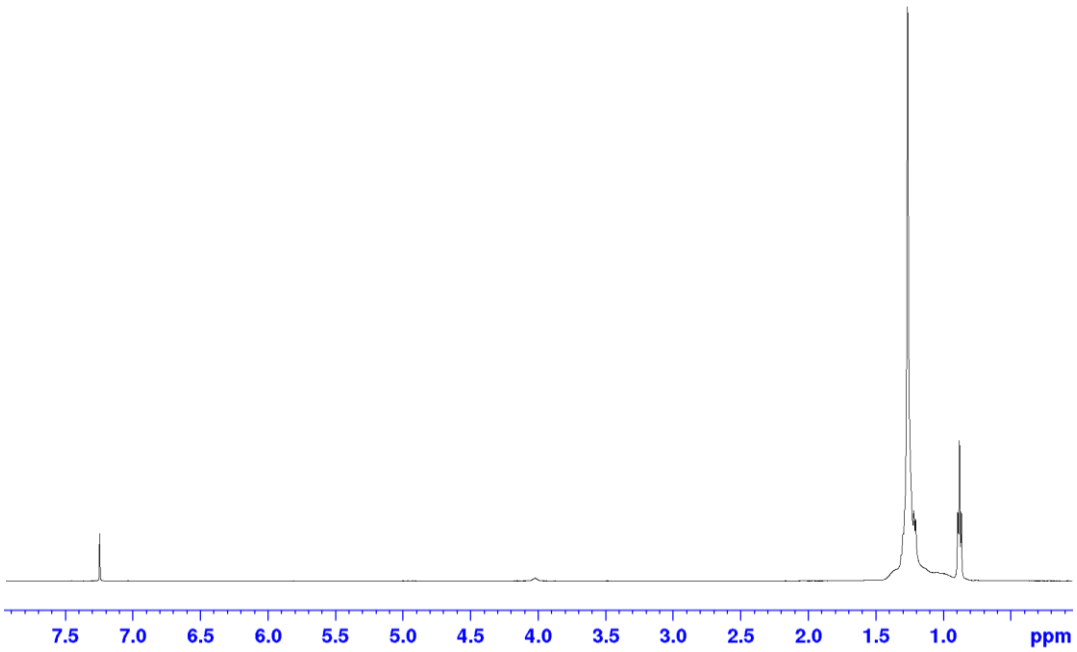

Figure S3-15. ^{1}H NMR spectrum in poly(1-dodecene) prepared by Cp*$TiCl_2$(O-2,6-$^{i}Pr_2C_6H_3$) - MAO catalyst (in $CDCl_3$ at 25 ºC, run S7, Table S1).

4. Selected DSC thermograms.

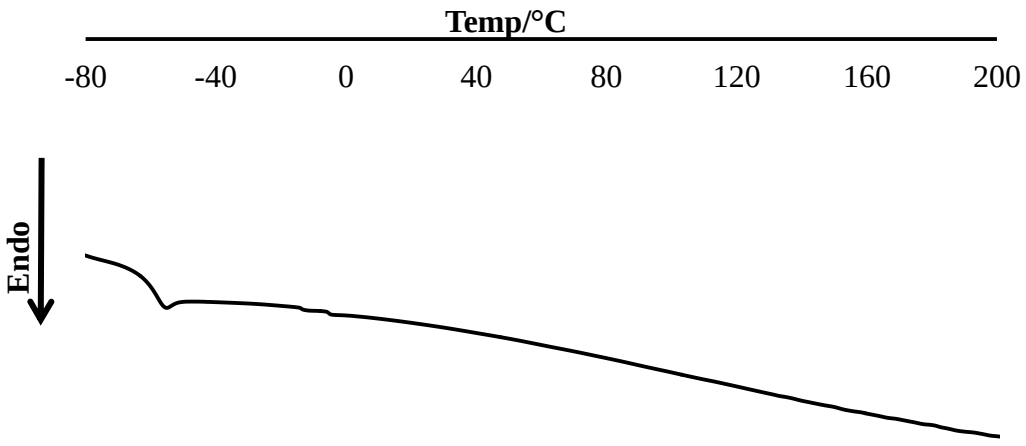

Figure S4-1. DSC thermogram in poly(1-octene) prepared by Cp^*TiCl_2 (O-2,6-$^{i}Pr_2C_6H_3$) - MAO catalyst (run 1, Table 1).

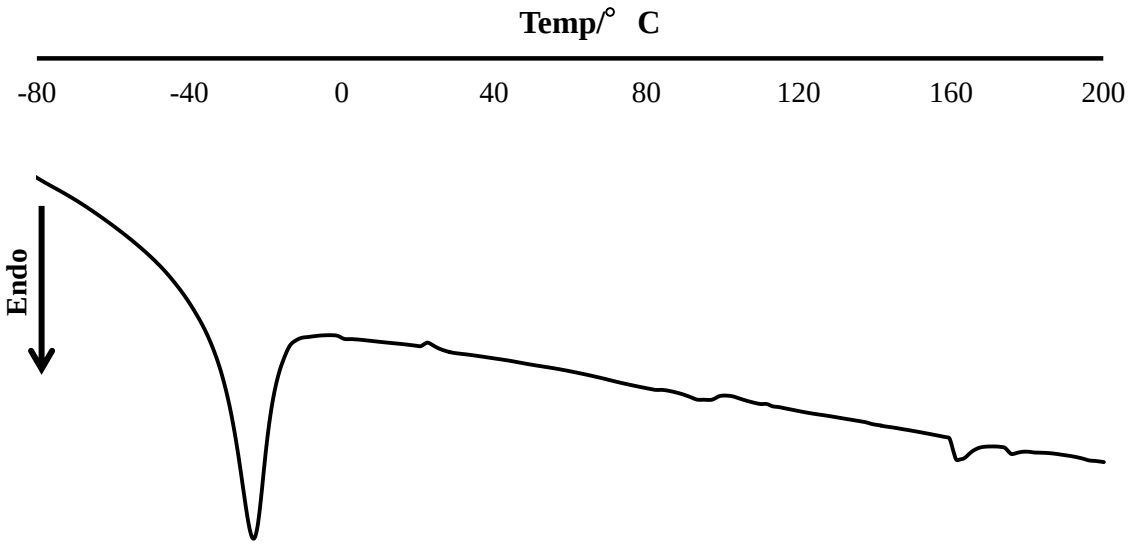

Figure S4-2. DSC thermogram in poly(1-dodecene) prepared by Cp^*TiCl_2 (O-2,6-$^{i}Pr_2C_6H_3$) - MAO catalyst (run 5, Table 1).

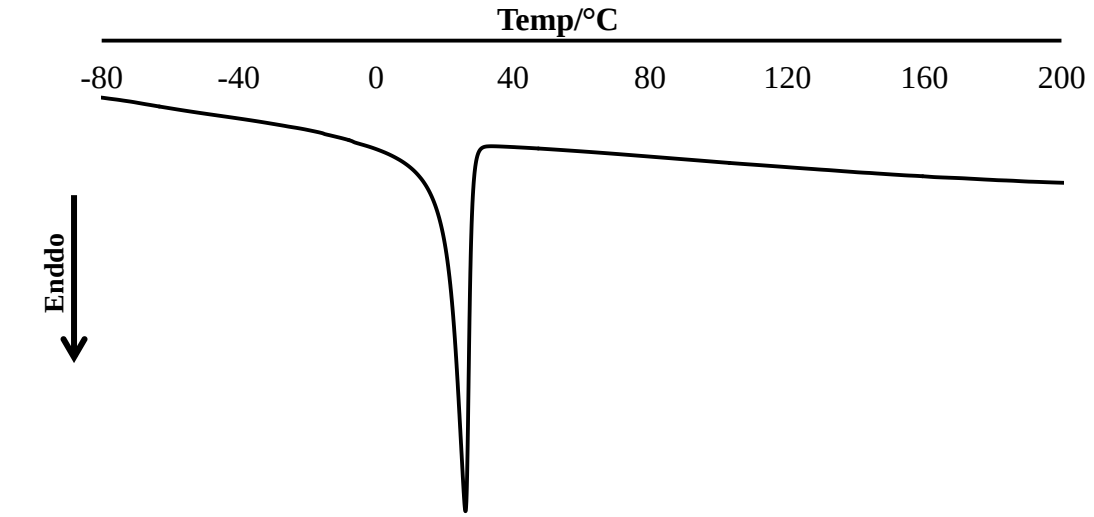

Figure S4-3. DSC thermogram in poly(1-hexadecene) prepared by Cp^*TiCl_2 (O-2,6-$^{i}Pr_2C_6H_3$) - MAO catalyst (run 6, Table 1).

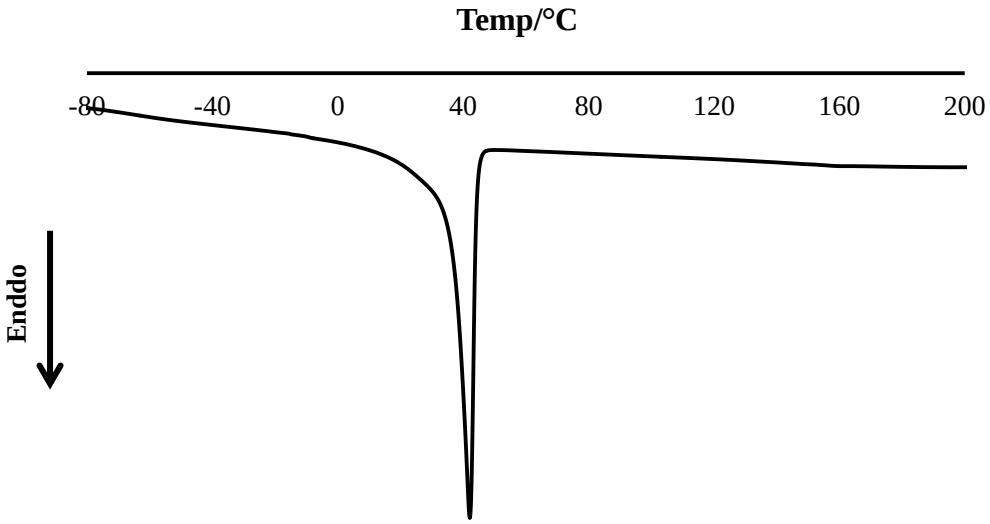

Figure S4-4. DSC thermogram in poly(1-octadecene) prepared by Cp^*TiCl_2 (O-2,6-$^{i}Pr_2C_6H_3$) - MAO catalyst (run 7, Table 1).

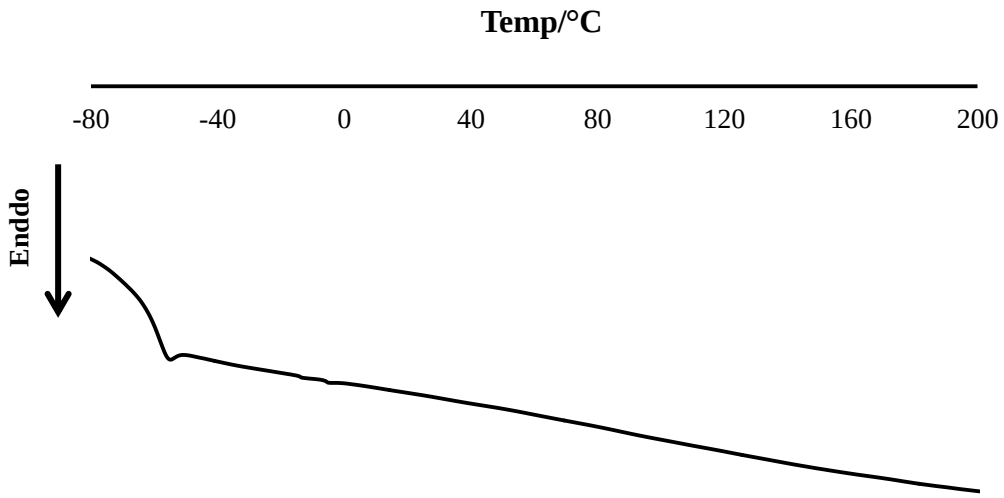

Figure S4-5. DSC thermogram in poly(1-octene) prepared by $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ - MAO catalyst (run 9, Table 1).

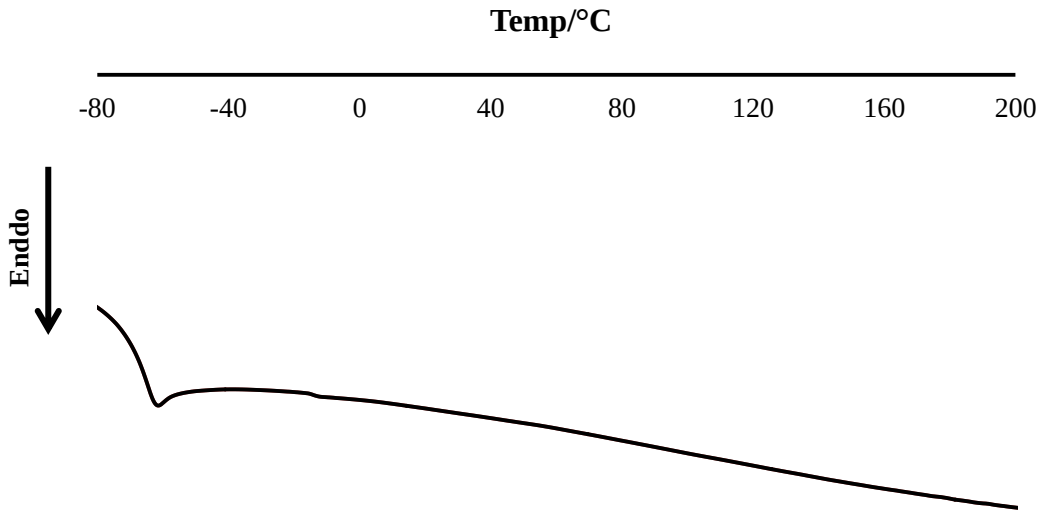

Figure S4-6. DSC thermogram in poly(1-decene) prepared by $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ - MAO catalyst (run 10, Table 1).

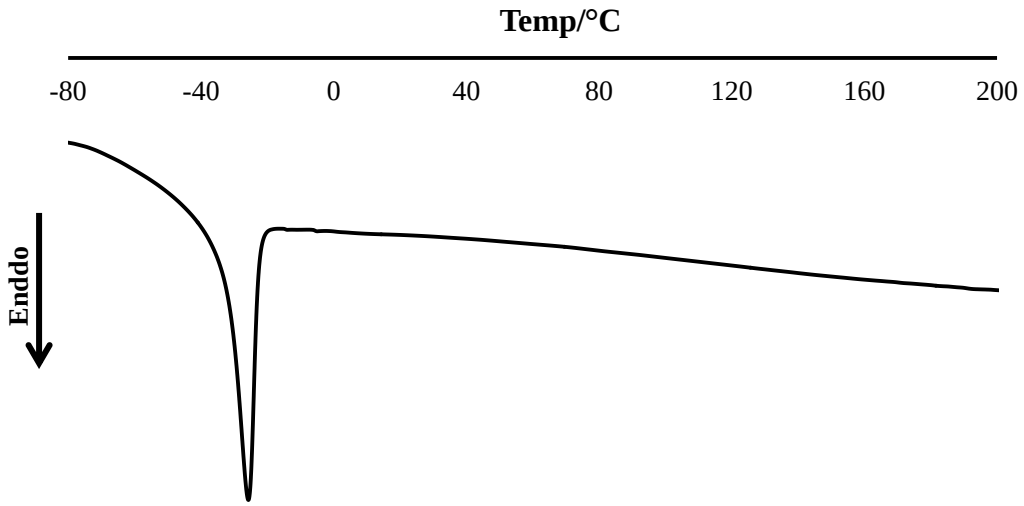

Figure S4-7. DSC thermogram in poly(1-dodecene) prepared by $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ - MAO catalyst system (run 12, Table 1).

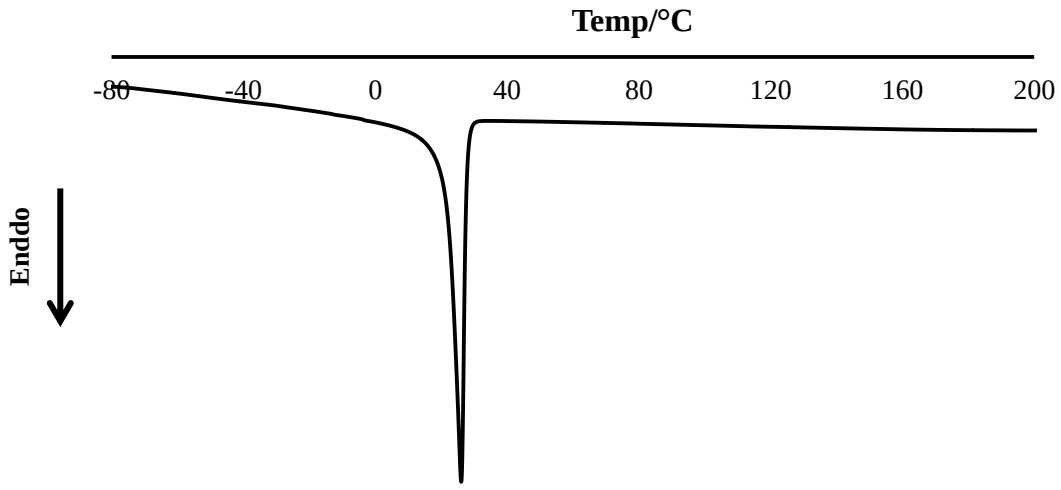

Figure S4-8. DSC thermogram in poly(1-hexadecene) prepared by $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ - MAO catalyst (run 13, Table 1).

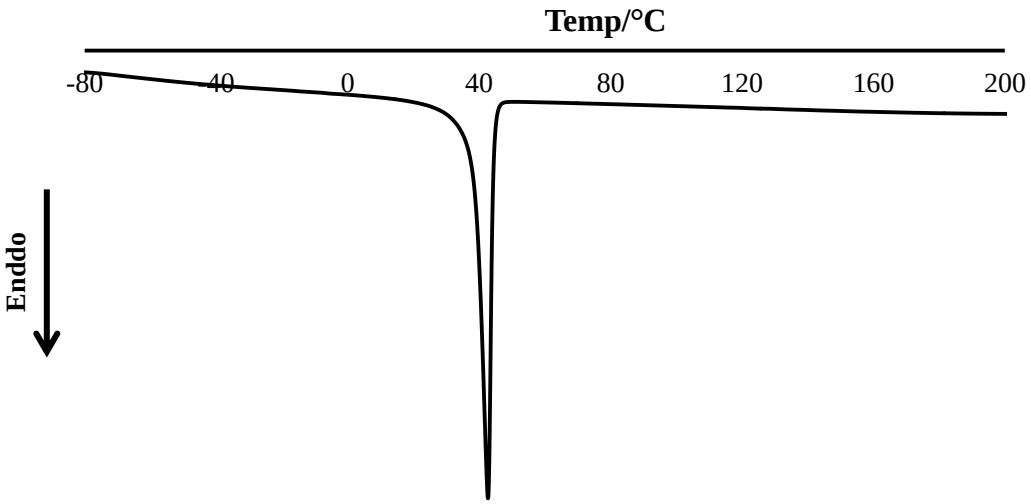

Figure S4-9. DSC thermogram in poly(1-octadecene) prepared by $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ - MAO catalyst (run 15, Table 1).

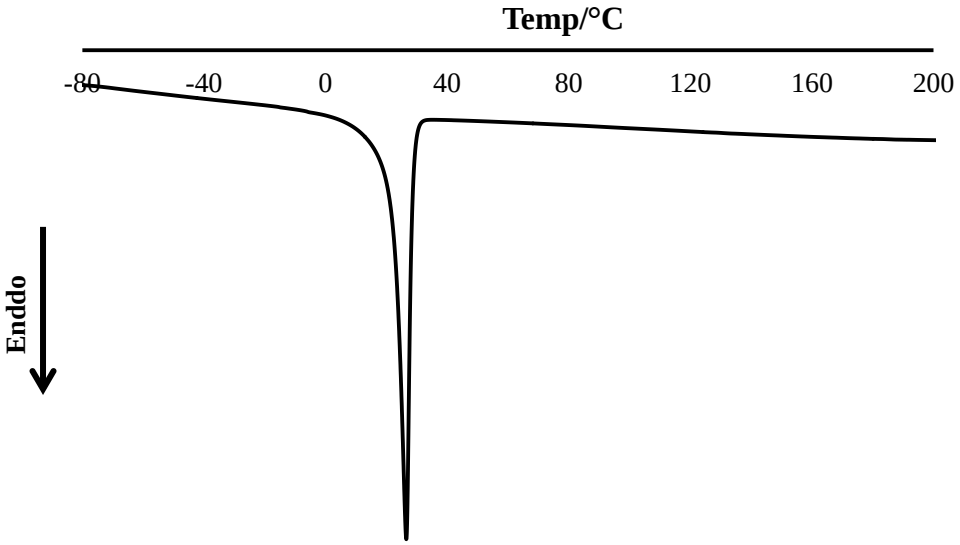

Figure S4-10. DSC thermogram in poly(1-hexadecene) prepared by Cp_2ZrCl_2 - MAO catalyst (run 20, Table 1).

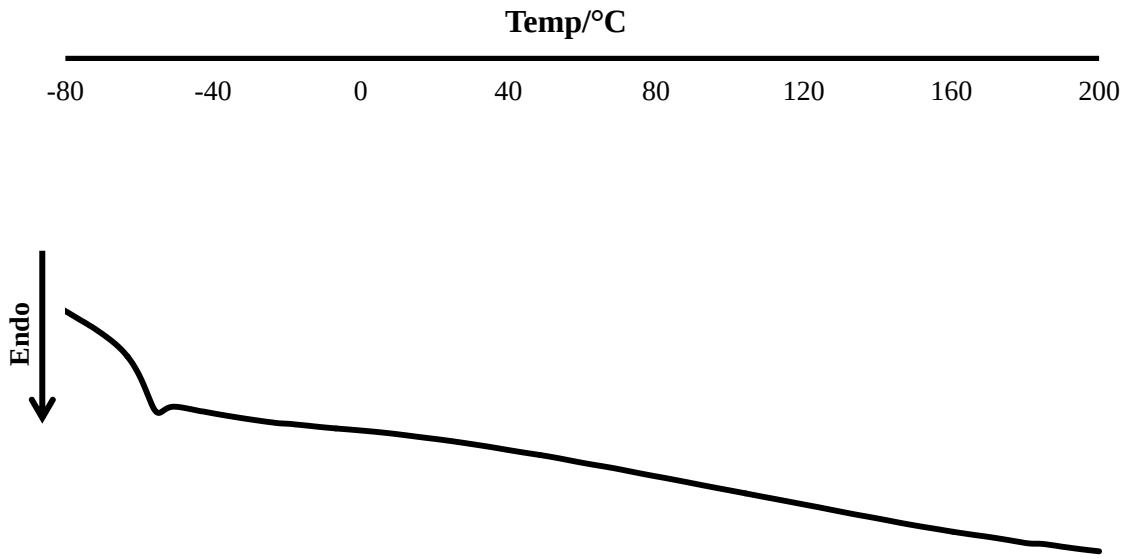

Figure S4-11. DSC thermogram in poly(1-octene) prepared by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) -borate catalyst (run 22, Table 2).

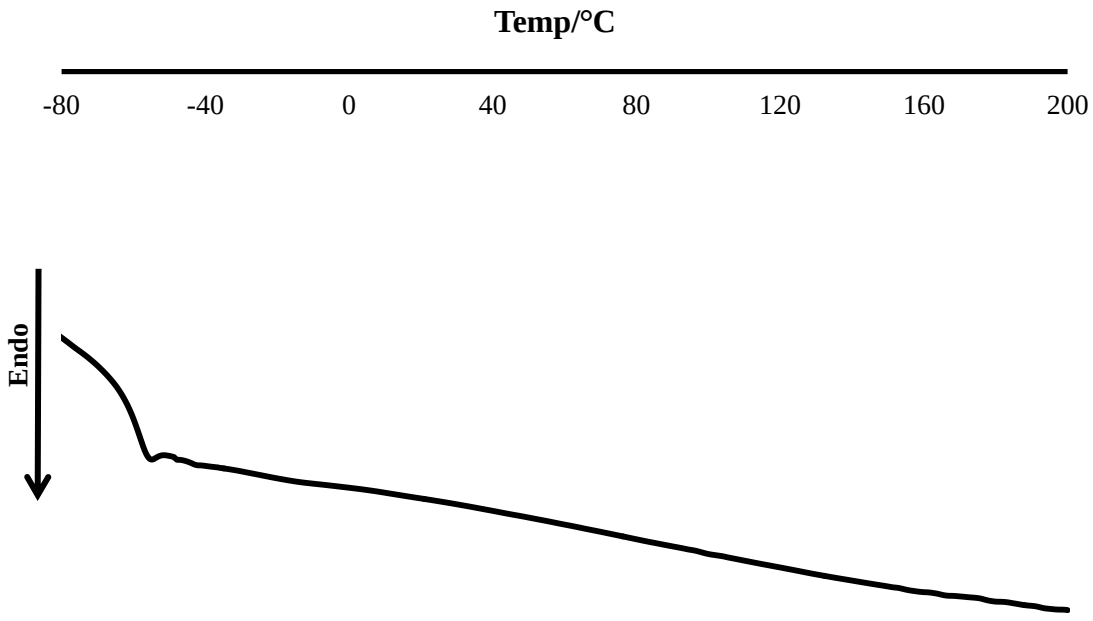

Figure S4-12. DSC thermogram in poly(1-octene) prepared by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) -borate catalyst (run 23, Table 2).

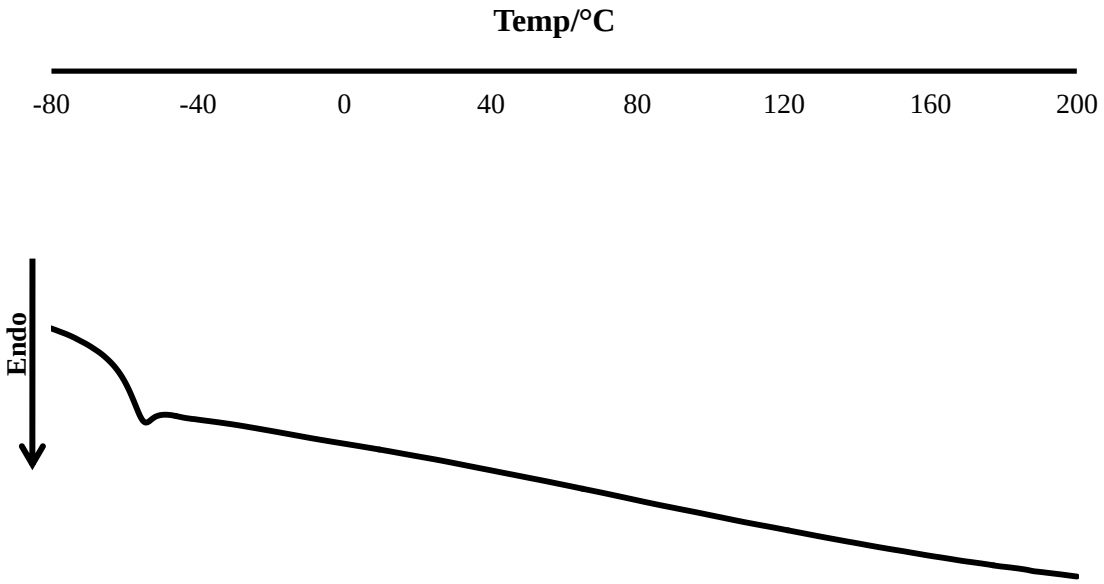

Figure S4-13. DSC thermogram in poly(1-octene) prepared by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) -borate catalyst (run 24, Table 2).

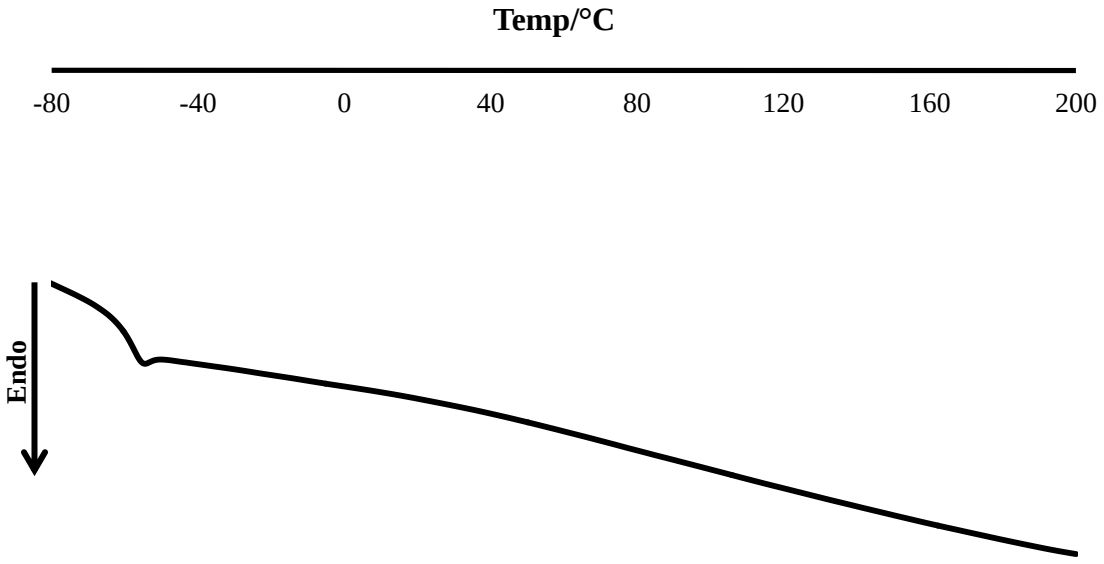

Figure S4-14. DSC thermogram in poly(1-octene) prepared by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) -borate catalyst (run 25, Table 2).

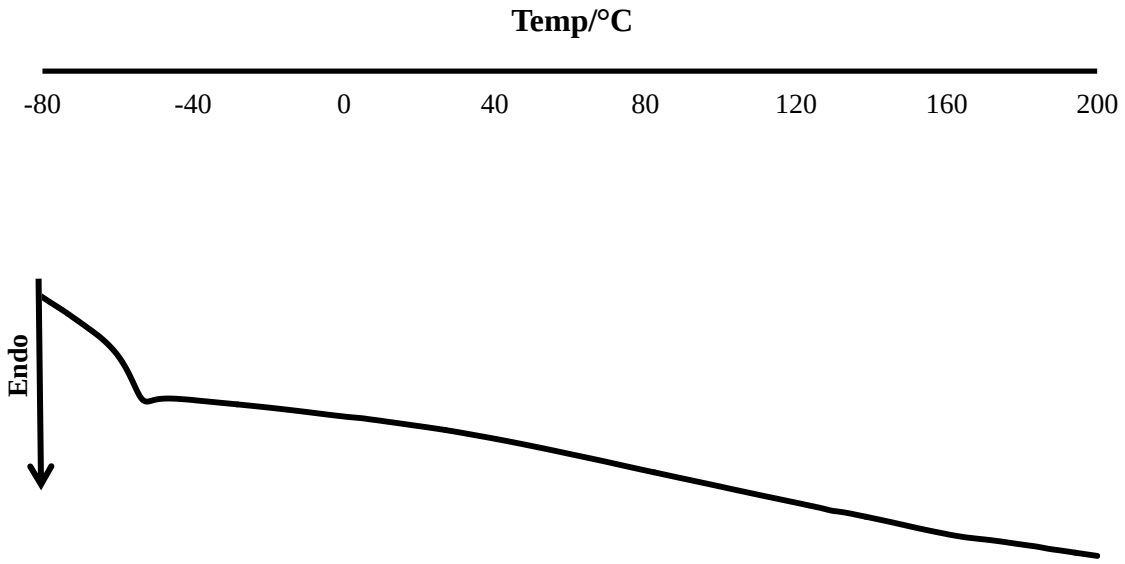

Figure S4-15. DSC thermogram in poly(1-octene) prepared by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) -borate catalyst (run 26, Table 2).

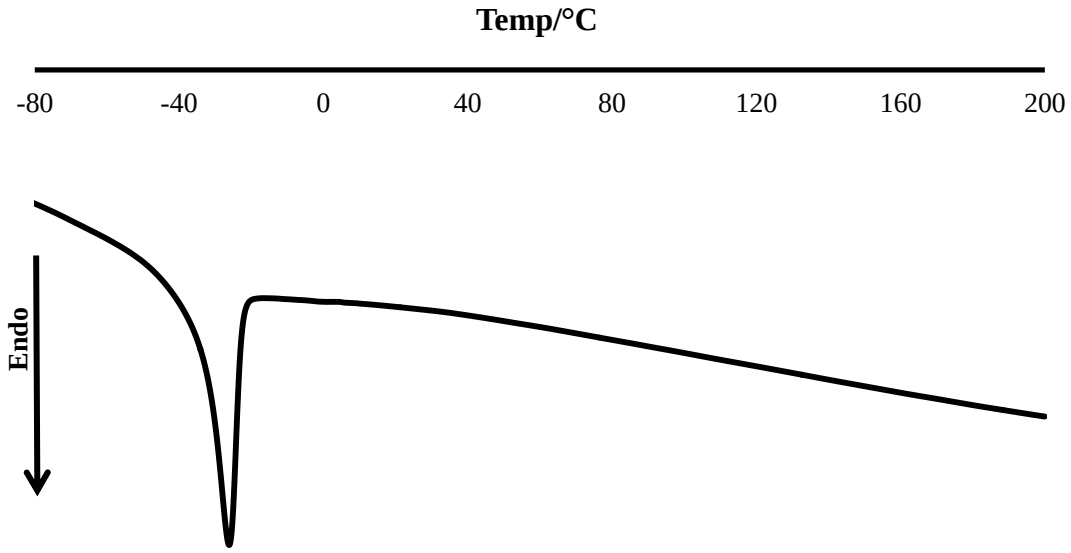

Figure S4-16. DSC thermogram in poly(1-dodecene) prepared by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) -borate catalyst (run 28, Table 2).