Electronic Supplementary Information

for

(Trialkylsilyl-cyclopentadienyl)titanium(IV) Dichloride Complexes Containing Ketimide Ligands, Cp'$TiCl_2$(N=C^tBu_2) (Cp' = $Me_3SiC_5H_4$, $Et_3SiC_5H_4$), as Efficient Catalysts for Ethylene Copolymerisations with Norbornene, Tetracyclododecene

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1. Crystal data and collection parameters of ($Me_3SiC_5H_4$)$TiCl_2$(N=C^tBu_2) (2), ($Et_3SiC_5H_4$)$TiCl_2$(N=C^tBu_2) (3).

Table S1. Crystal data and collection parameters of ($Me_3SiC_5H_4$)$TiCl_2$(N=C^tBu_2) (**2**), ($Et_3SiC_5H_4$)$TiCl_2$(N=C^tBu_2) (**3**).

	2	**3**
CCDC No.	CCDC2353042	CCDC2353043
Formula	$C_{17}H_{31}Cl_2NSiTi$	$C_{20}H_{37}Cl_2NSiTi$
Formula weight	396.29	438.37
Crystal color, Habit	red, plate	violet, needle
Crystal size (mm)	0.172 × 0.067 × 0.024	0.243 × 0.03 × 0.02
Crystal system	triclinic	orthorhombic
Space group	P-1	$P2_12_12_1$
a (Å)	6.6617(2)	12.2674(4)
b (Å)	17.3131(4)	13.7760(4)
c (Å)	28.1245(10)	14.0063(4)
α (deg)	93.203(2)	
β (deg)	92.284(3)	
γ (deg)	95.465(2)	
V (Å^3)	3220.61(17)	2367.00(12)
Z value	6	4
D_{calcd} (g/cm^3)	1.226	1.230
F_{000}	1260	936
Temp (K)	123(2)	123(2)
μ (Mo Kα) (cm^{-1})	7.10	6.42
No. of reflections measured (R_{int})	49309	35494
$2\theta_{max}$ (deg)	56.5	56.4
No. of observations [$I > 2.00\sigma(I)$]	15913	5835
No. of variables	622	235
$R1$ [$I > 2.00\sigma(I)$]	0.0561	0.0460
$wR2$ [$I > 2.00\sigma(I)$]	0.1359	0.1109
Goodness of Fit	1.073	1.044

2. NMR spectra for $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (2) and $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (3)

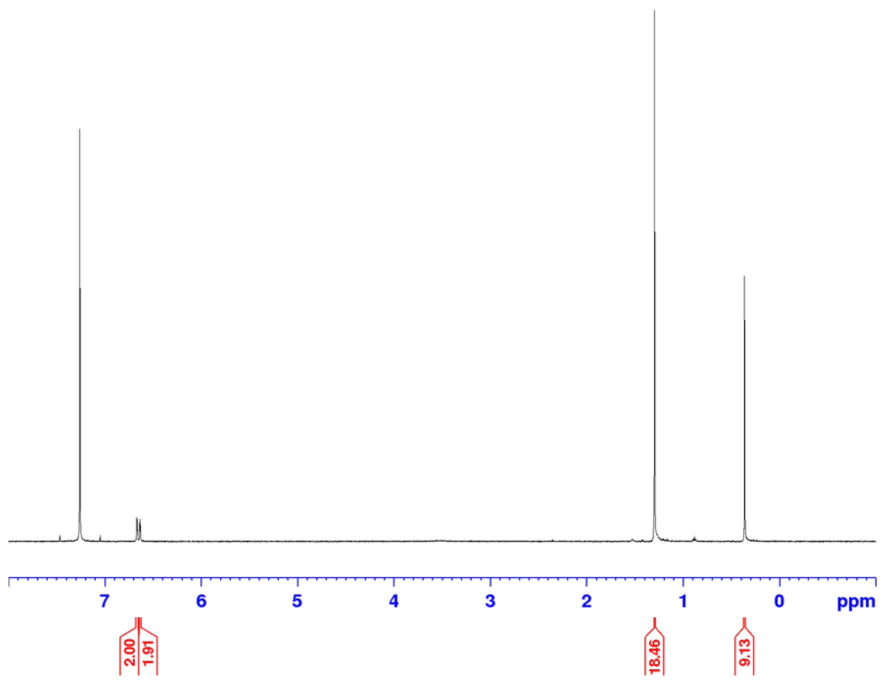

Figure S1. ^{1}H NMR spectrum of $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**) (in $CDCl_3$ at 25 ºC).

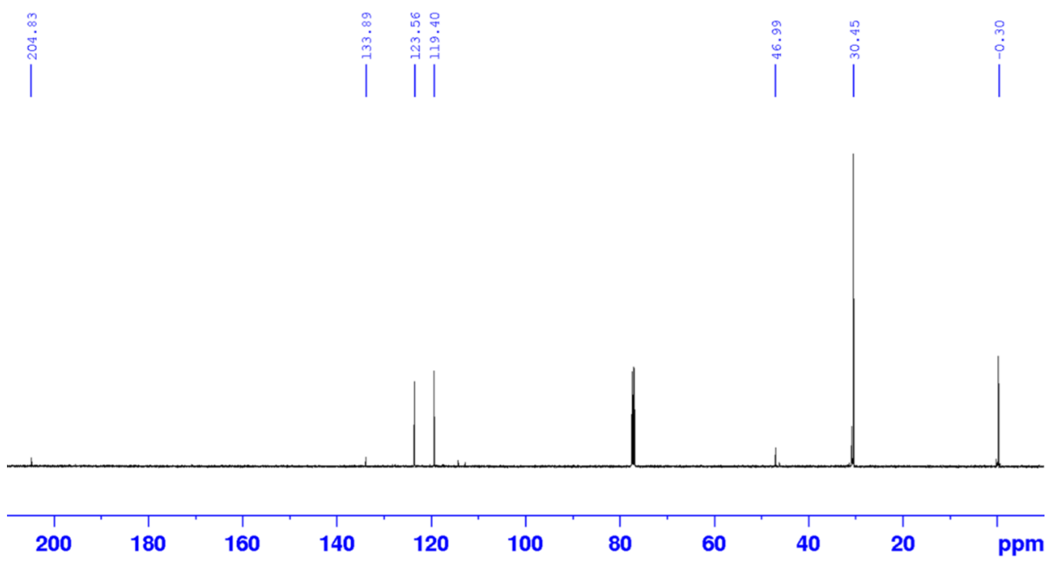

Figure S2. $^{13}C\{^1H\}$ NMR spectrum of $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**) (in $CDCl_3$ at 25 ºC).

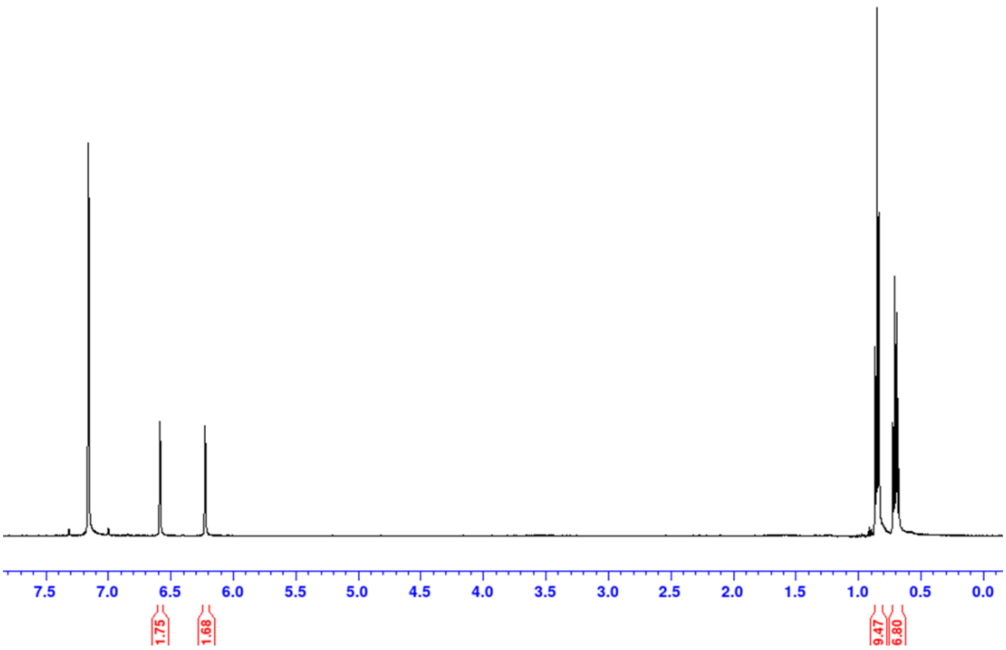

Figure S3. [1]H NMR spectrum of $(Et_3SiC_5H_4)TiCl_3$ (in C_6D_6 at 25 ºC).

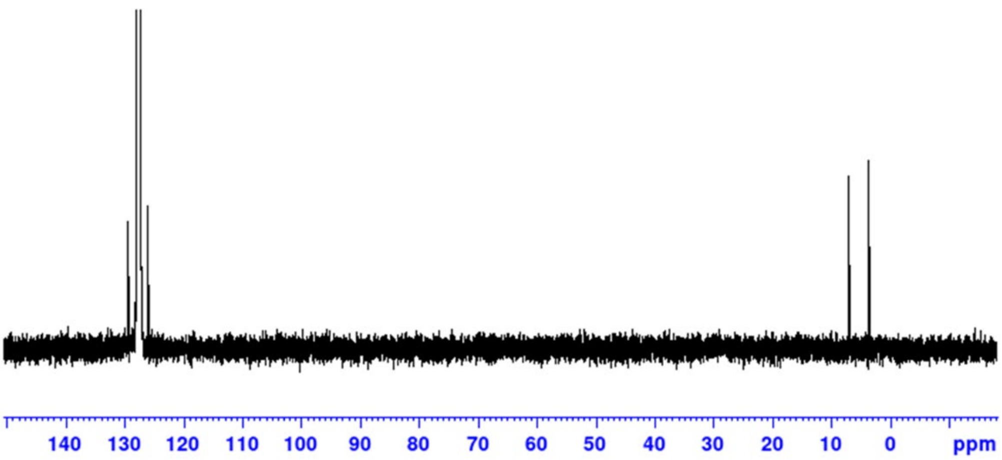

Figure S4. $^{13}C\{^1H\}$ NMR spectrum of $(Et_3SiC_5H_4)TiCl_3$ (in C_6D_6 at 25 ºC).

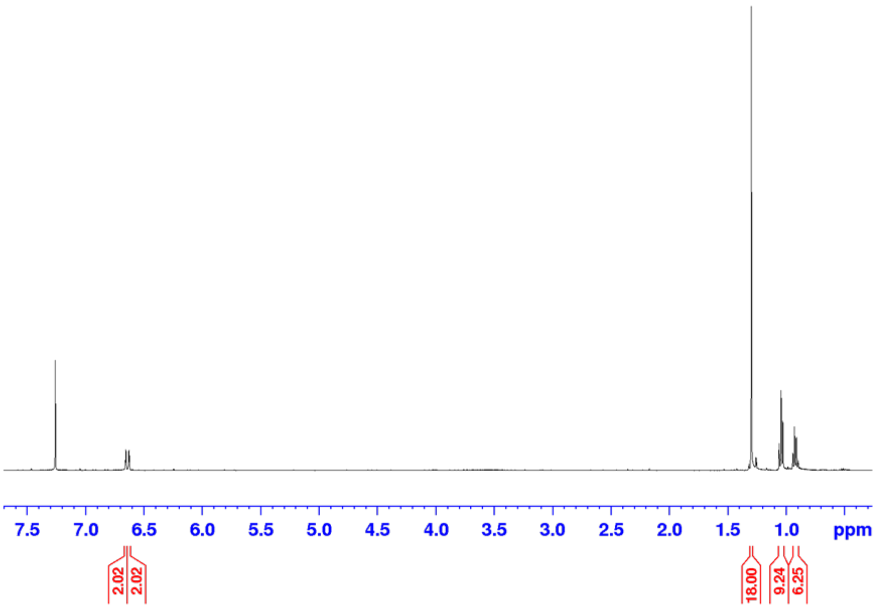

Figure S5. [1]H NMR spectrum of $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) (in $CDCl_3$ at 25 ºC).

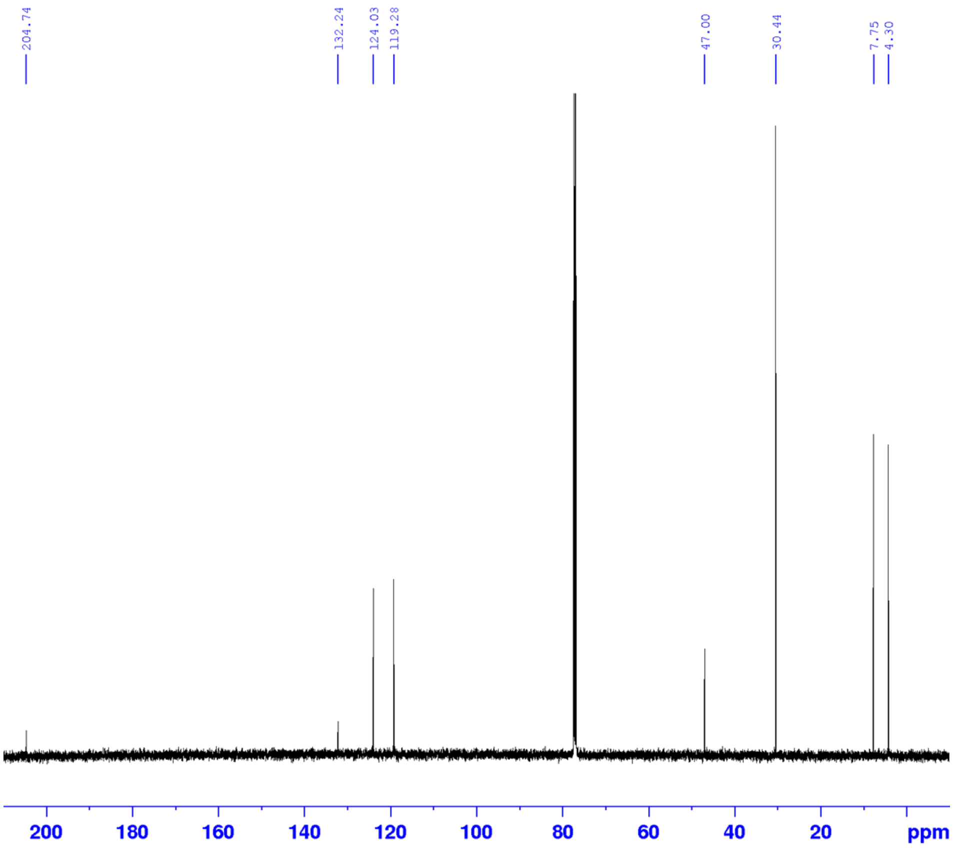

Figure S6. [13]C{[1]H} NMR spectrum of $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) (in $CDCl_3$ at 25 ºC).

3. Selected ^{13}C NMR spectra of the resultant copolymers

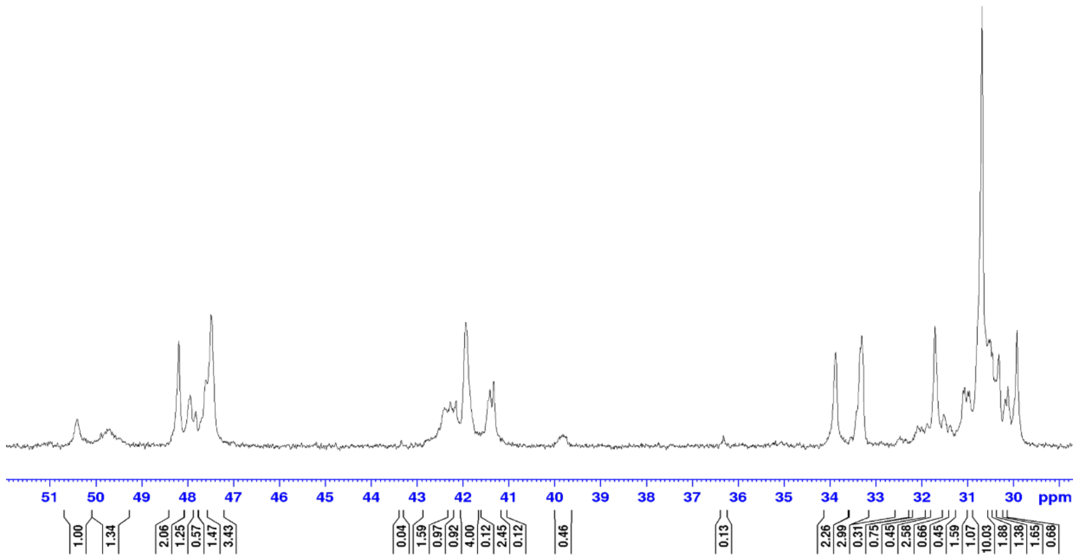

Figure S7. $^{13}C\{^1H\}$ NMR spectrum in poly(ethylene-*co*-norbornene) prepared by $(Me_3SiC_5H_4)$-$TiCl_2(N{=}C^tBu_2)$ (**2**)–MAO catalyst (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C, run 8, Table 2).

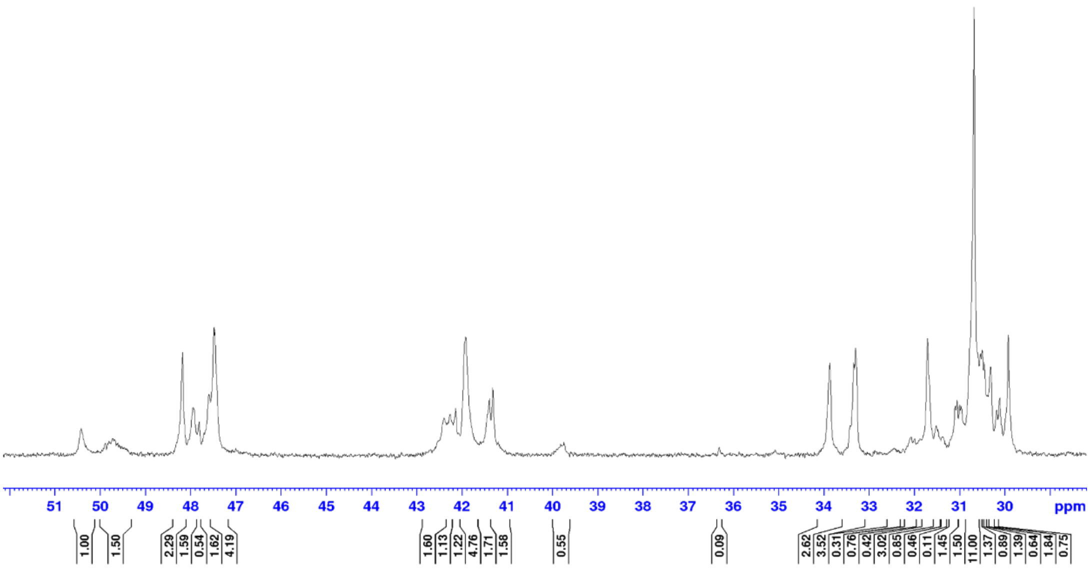

Figure S8. $^{13}C\{^1H\}$ NMR spectrum in poly(ethylene-*co*-norbornene) prepared by $(Me_3SiC_5H_4)$-$TiCl_2(N{=}C^tBu_2)$ (**2**)–MAO catalyst (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C, run 9, Table 2).

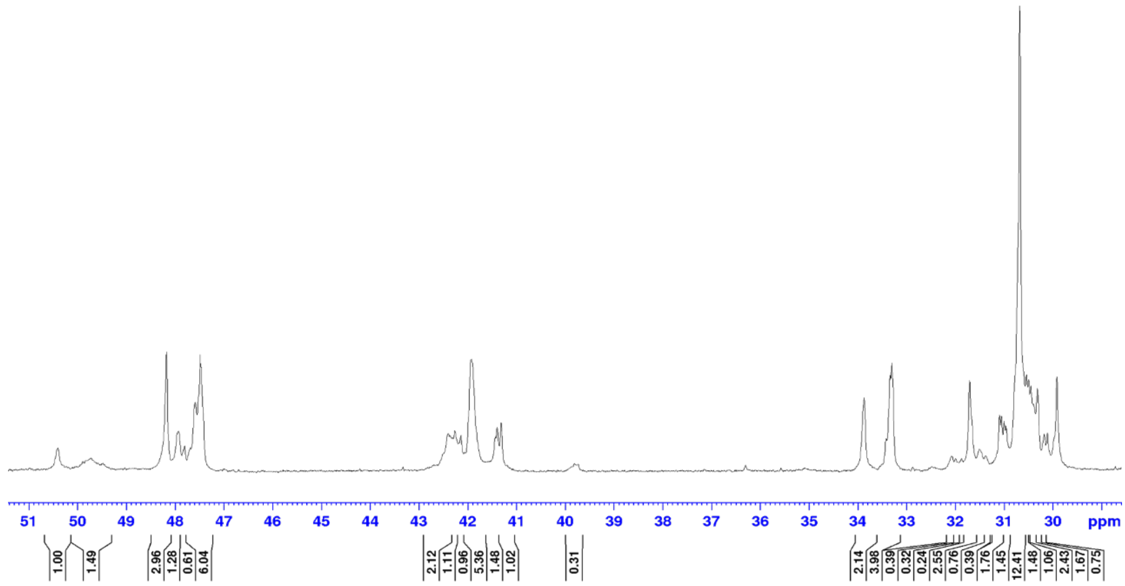

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum in poly(ethylene-*co*-norbornene) prepared by $(Me_3SiC_5H_4)$-$TiCl_2(N{=}C^{t}Bu_2)$ (**2**)–MAO catalyst (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C, run 11, Table 2).

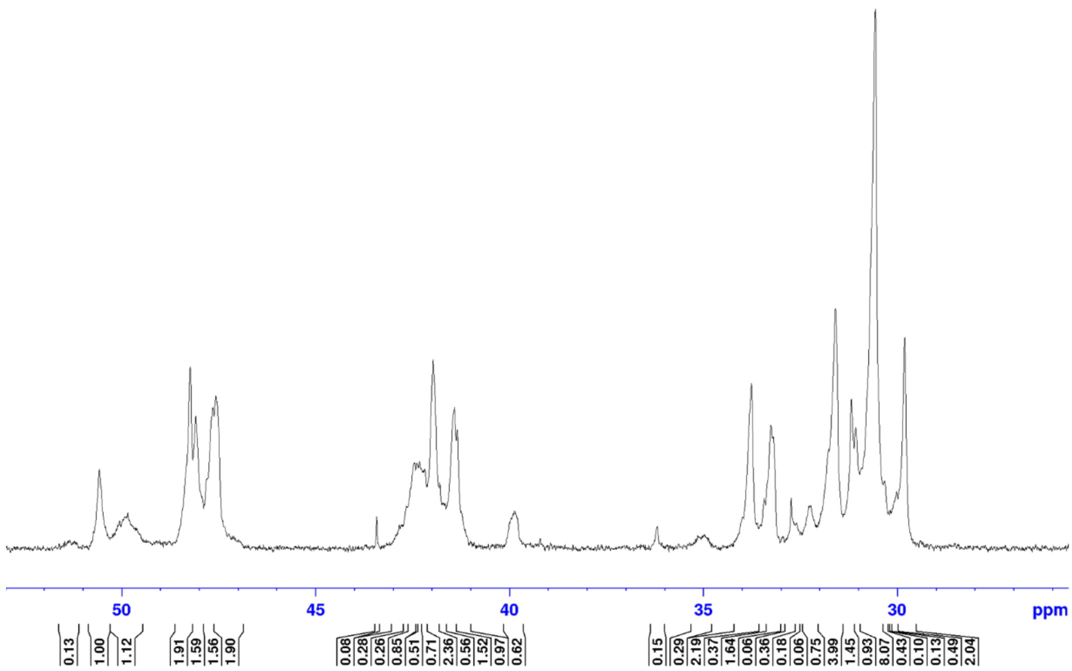

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum in poly(ethylene-*co*-norbornene) prepared by $(Et_3SiC_5H_4)$-$TiCl_2(N{=}C^{t}Bu_2)$ (**3**)–MAO catalyst (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C, run 21, Table 2).

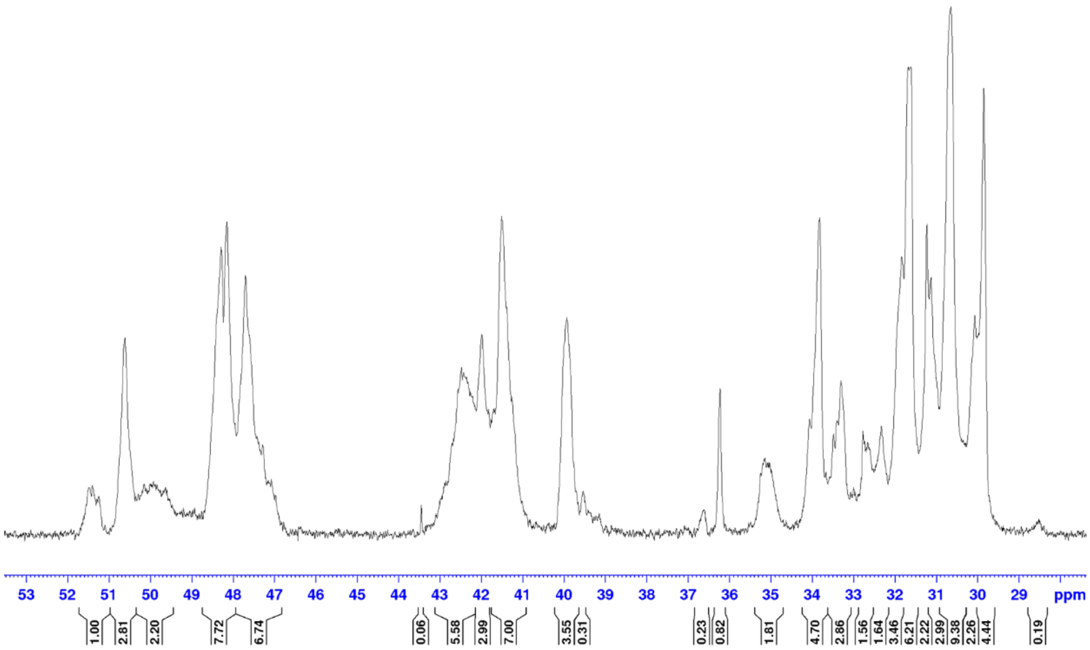

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum in poly(ethylene-*co*-norbornene) prepared by $(Et_3SiC_5H_4)$-$TiCl_2(N{=}C^tBu_2)$ (**3**)–MAO catalyst (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C, run 28, Table 2).

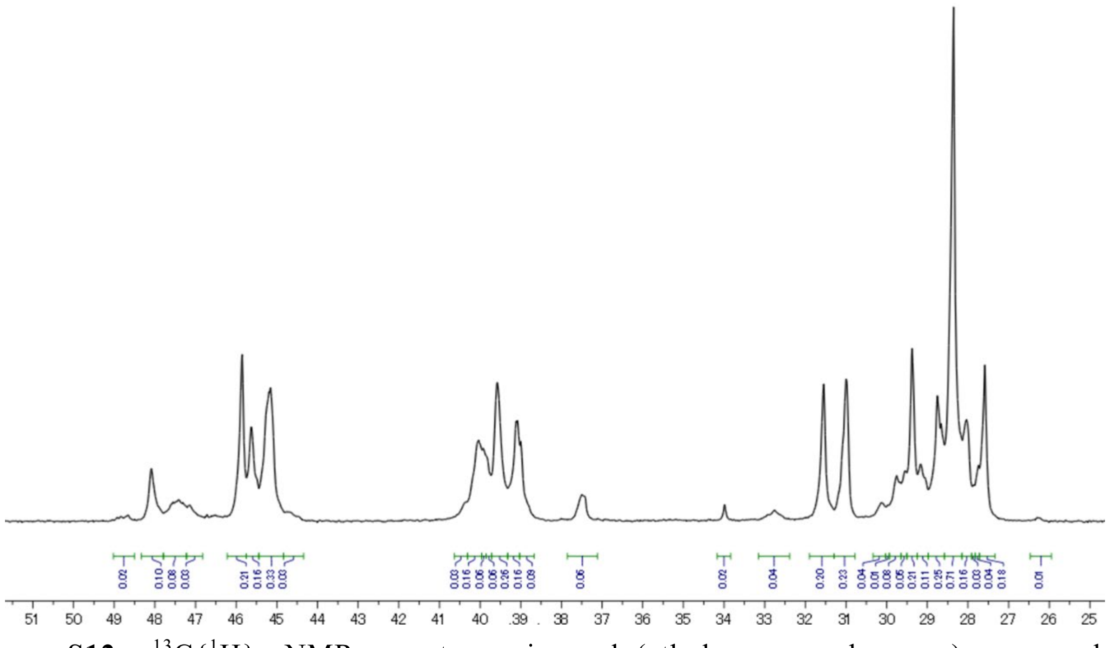

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum in poly(ethylene-*co*-norbornene) prepared by $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**)–MAO catalyst (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C, run 31, Table 3).

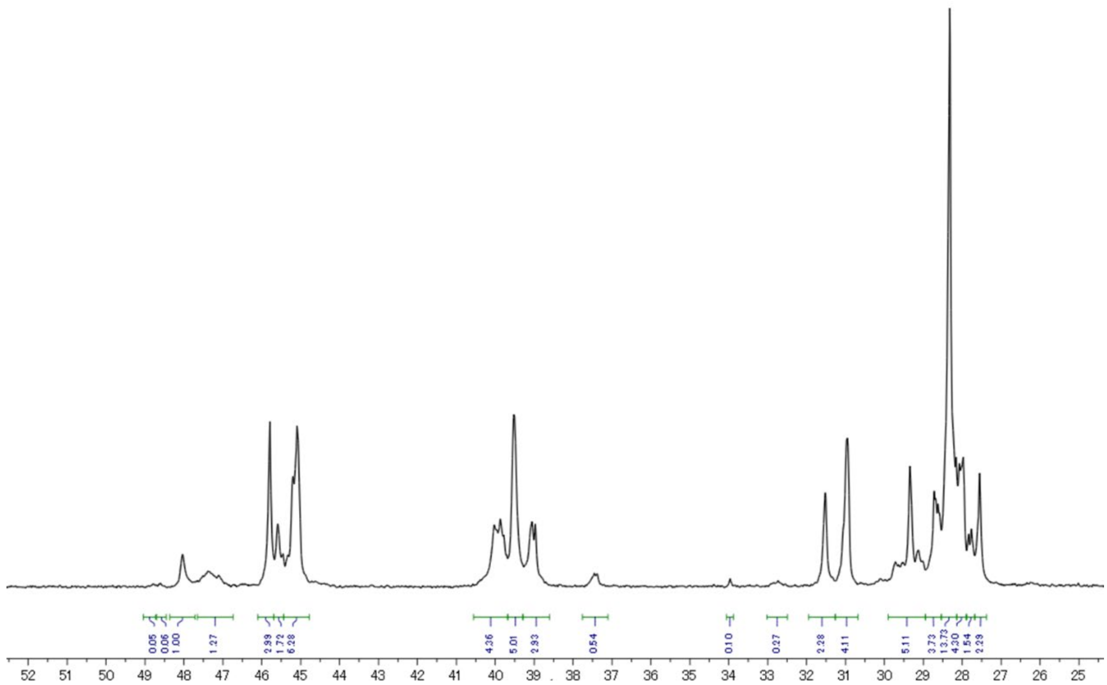

Figure S13. $^{13}C\{^1H\}$ NMR spectrum in poly(ethylene-*co*-norbornene) prepared by $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**)–MAO catalyst (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C, run 32, Table 3).

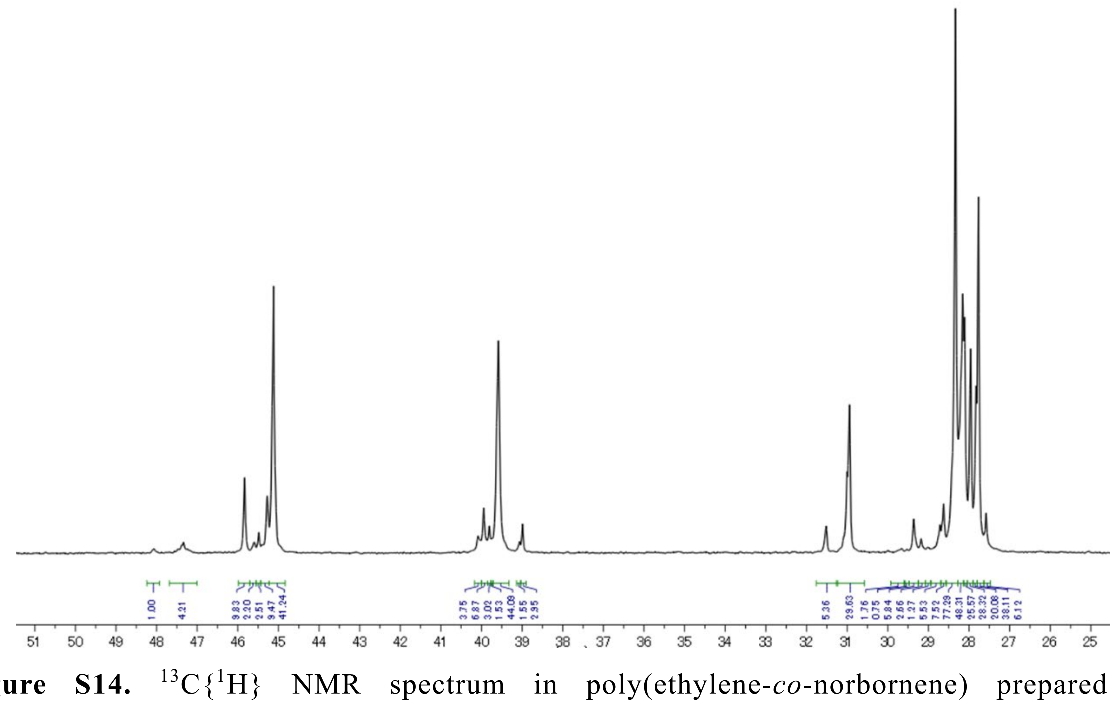

Figure S14. $^{13}C\{^1H\}$ NMR spectrum in poly(ethylene-*co*-norbornene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**)–MAO catalyst (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C, run 33, Table 3).

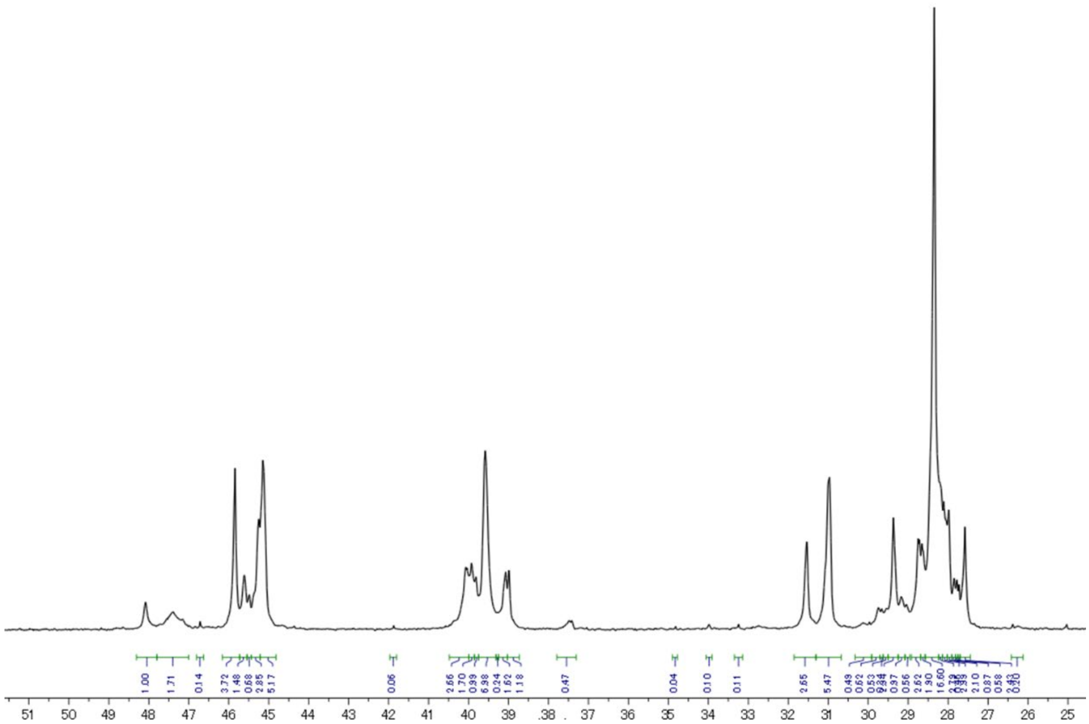

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum in poly(ethylene-*co*-norbornene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**)–MAO catalyst (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C, run 35, Table 3).

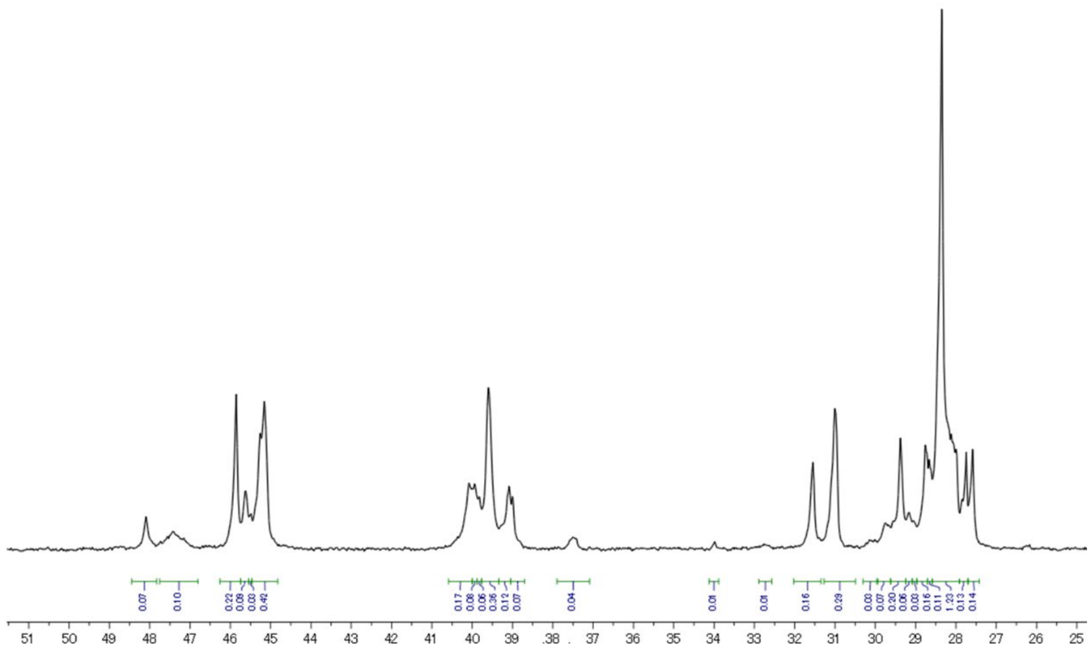

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum in poly(ethylene-*co*-norbornene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**)–MAO catalyst (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C, run 36, Table 3).

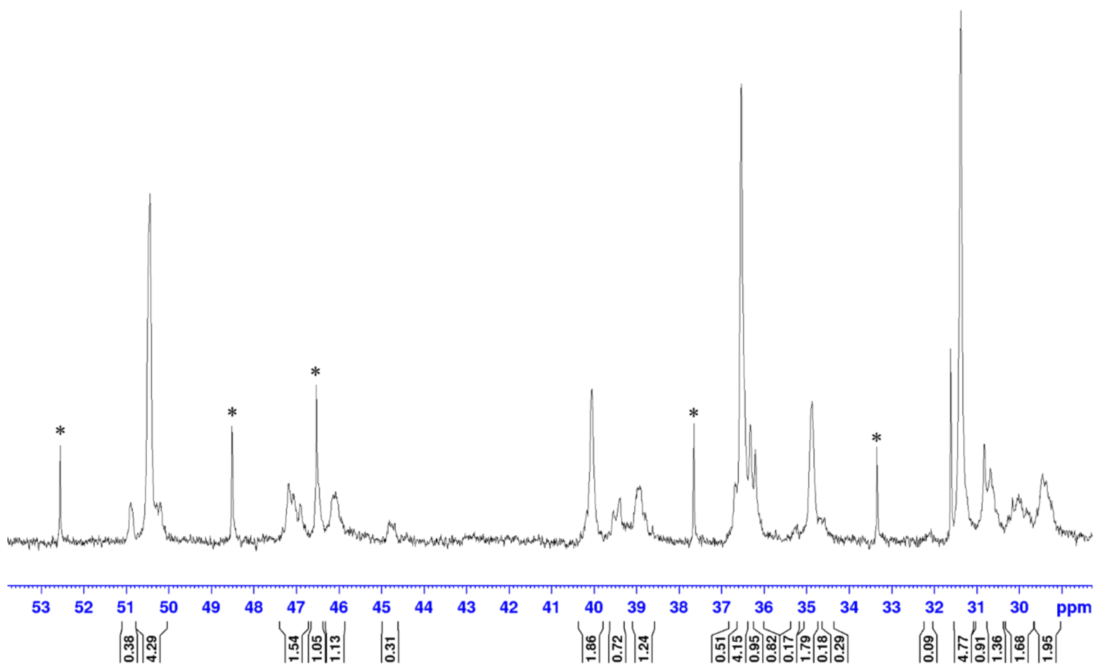

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum in poly(ethylene-*co*-tetracyclododecene) prepared by $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**)–MAO catalyst (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C, run 39, Table 4). *TCD contaminated in the copolymer as impurities.

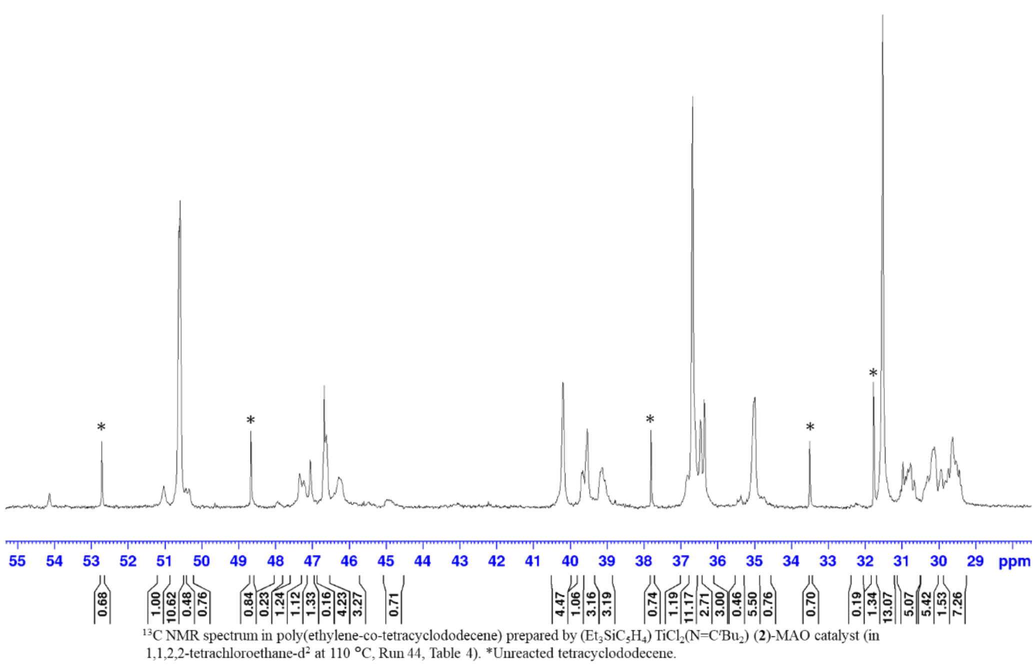

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum in poly(ethylene-*co*-tetracyclododecene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**)–MAO catalyst (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C, run 44, Table 4). *TCD contaminated in the copolymer as impurities.

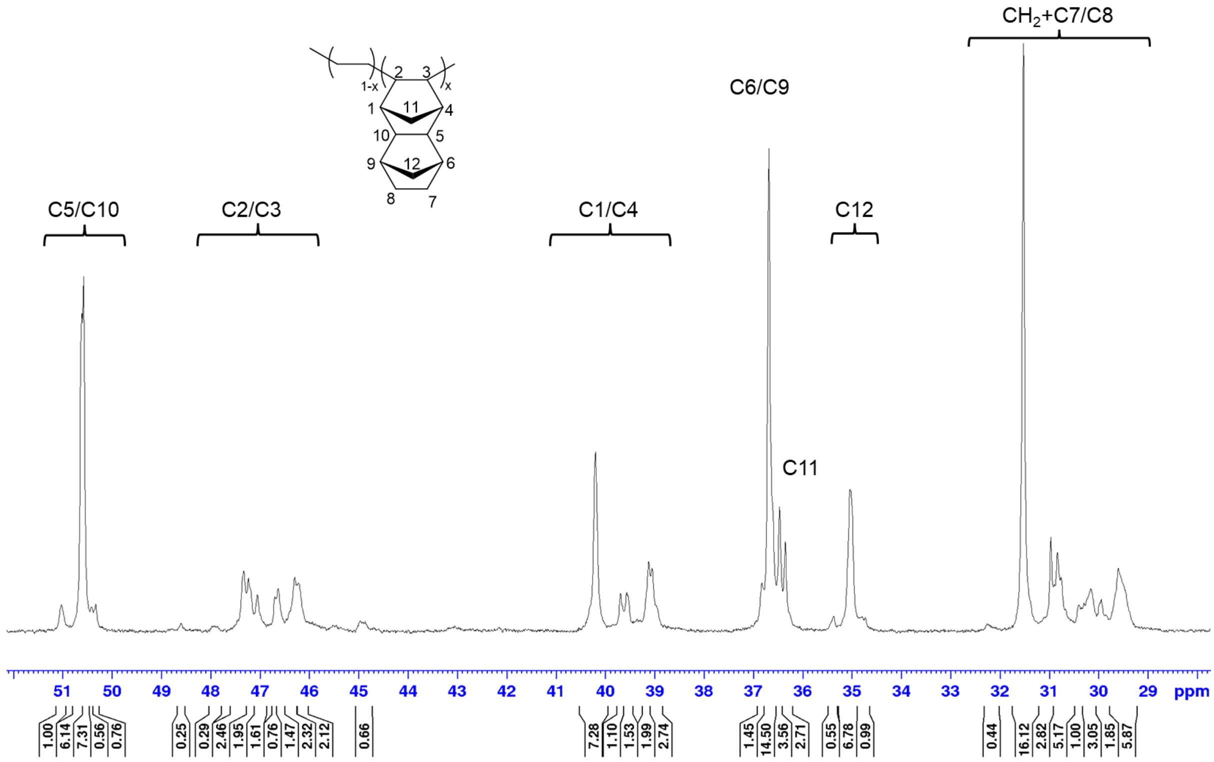

Figure S19. $^{13}C\{^1H\}$ NMR spectrum in poly(ethylene-*co*-tetracyclododecene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**)–MAO catalyst (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C, run 54, Table 4).

4. Selected DSC thermograms in the resultant copolymers

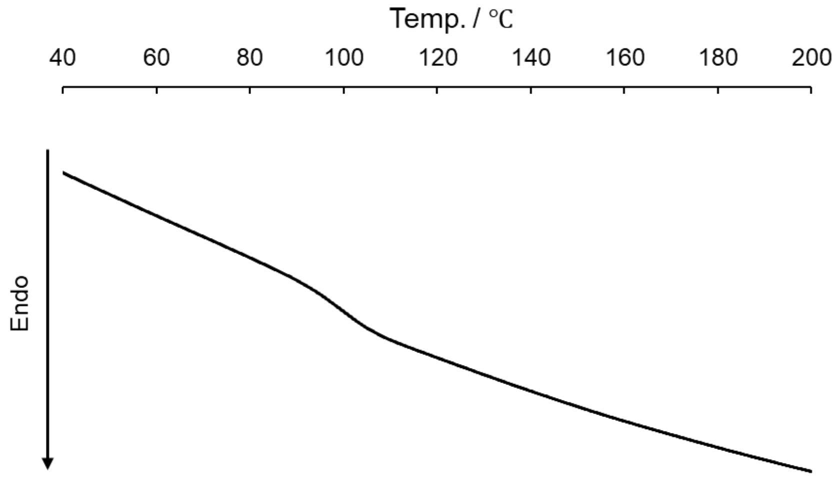

Figure S20. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by ($Me_3SiC_5H_4$)$TiCl_2$(N=C^tBu_2) (**2**) – MAO catalyst system (run 8).

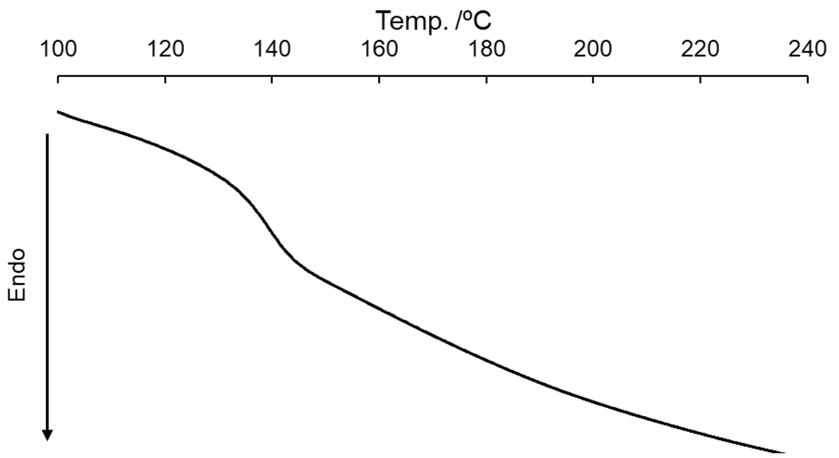

Figure S21. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by ($Me_3SiC_5H_4$)$TiCl_2$(N=C^tBu_2) (**2**) – MAO catalyst system (run 9).

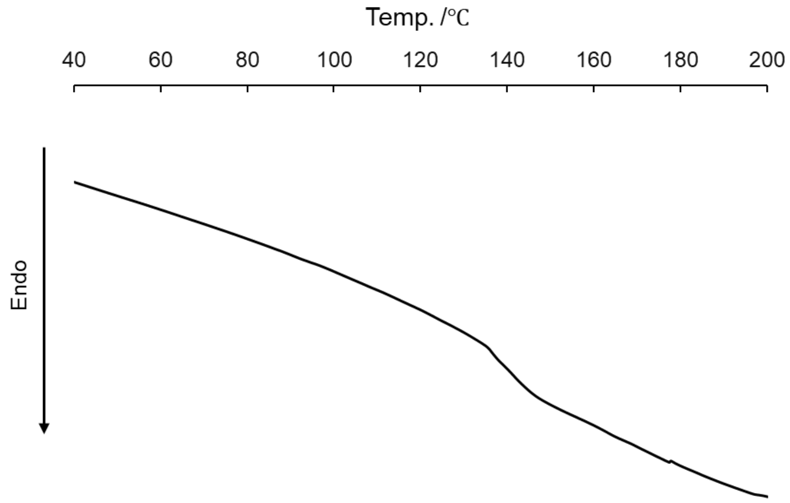

Figure S22. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**) – MAO catalyst system (run 12).

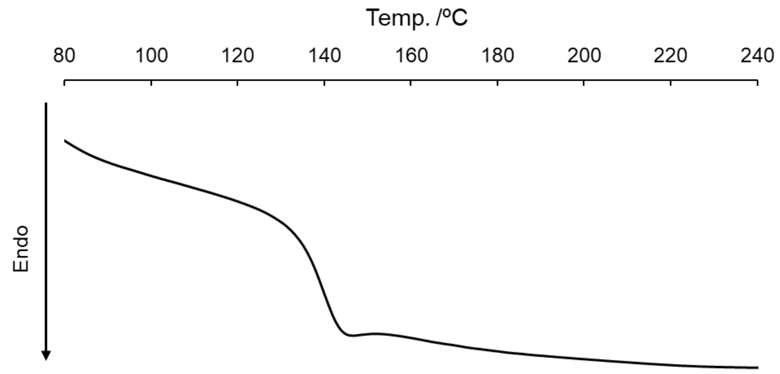

Figure S23. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**) – MAO catalyst system (run 13).

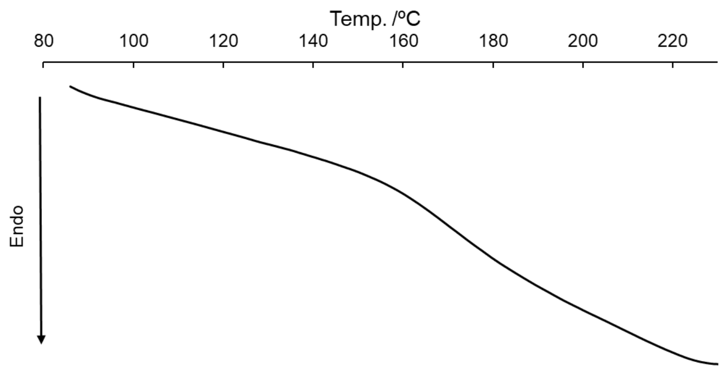

Figure S24. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**) – MAO catalyst system (run 14).

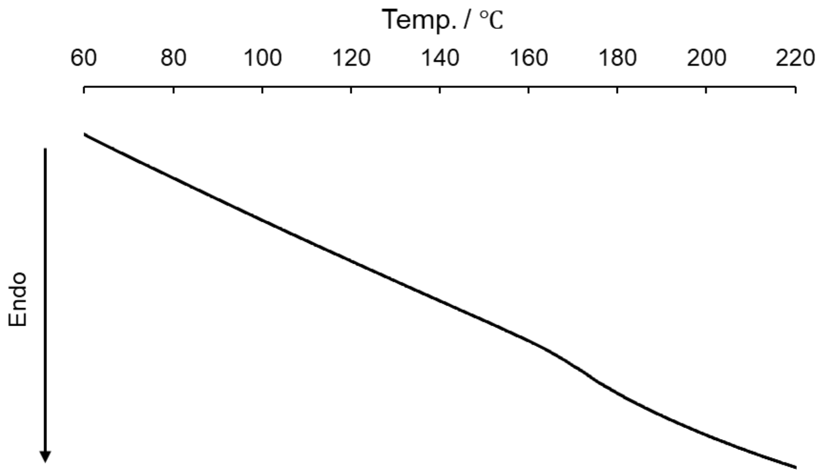

Figure S25. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by ($Me_3SiC_5H_4$)$TiCl_2$(N=C^tBu_2) (**2**) – MAO catalyst system (run 15).

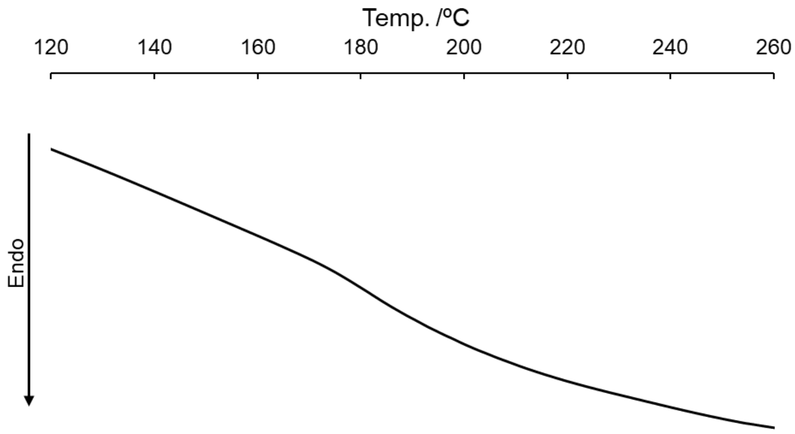

Figure S26. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by ($Me_3SiC_5H_4$)$TiCl_2$(N=C^tBu_2) (**2**) – MAO catalyst system (run 16).

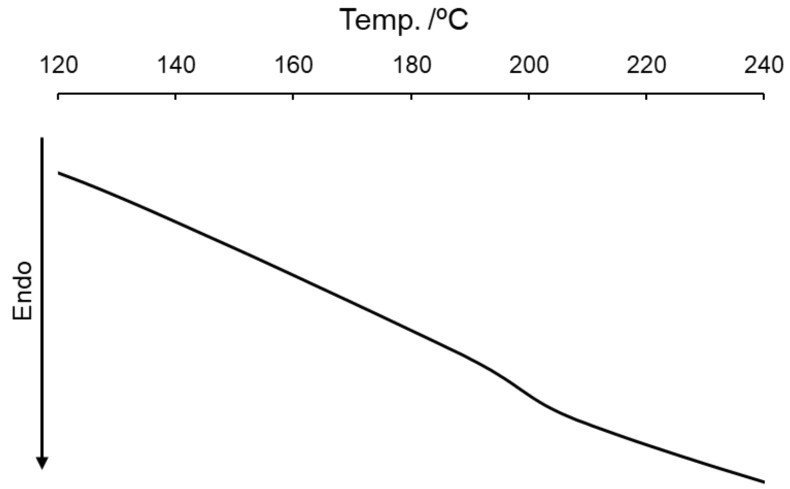

Figure S27. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**) – MAO catalyst system (run 17).

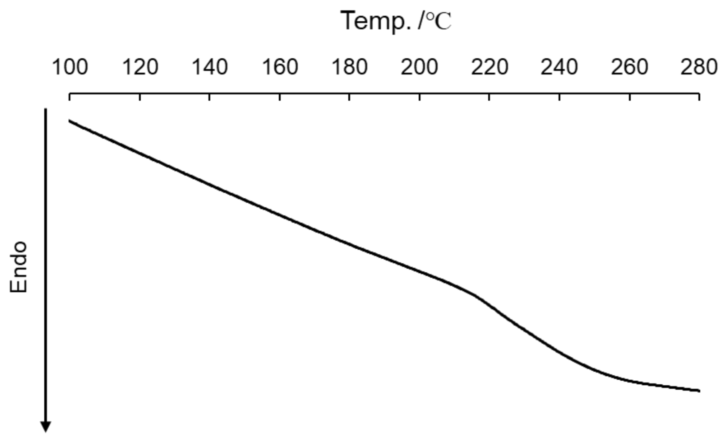

Figure S28. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**) – MAO catalyst system (run 18).

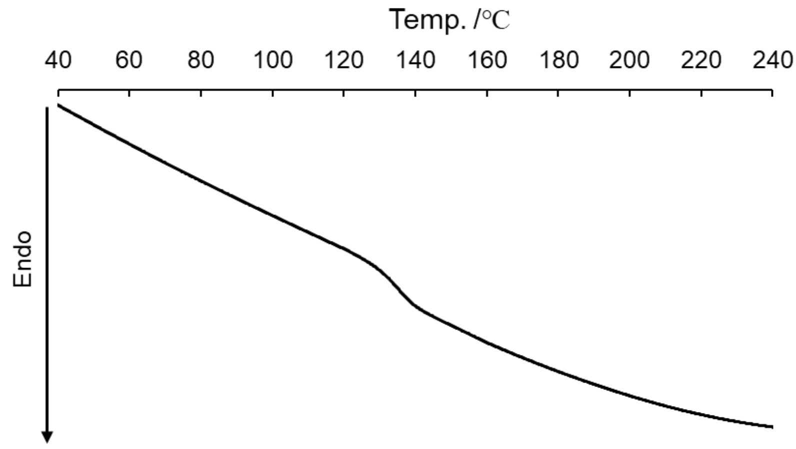

Figure S29. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) – MAO catalyst system (run 21).

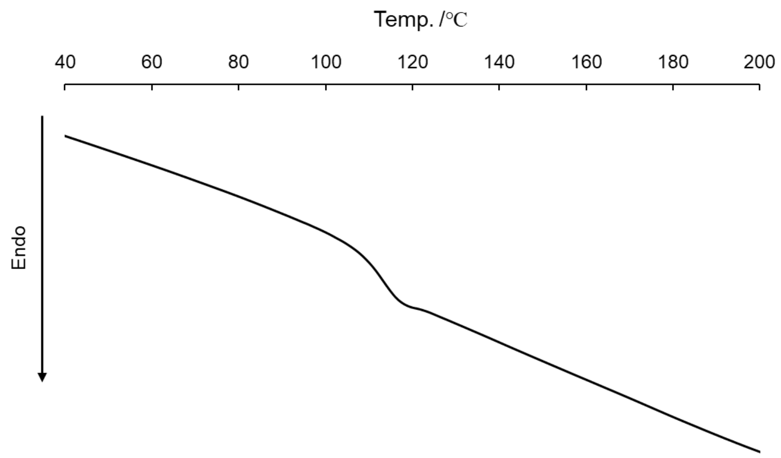

Figure S30. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) – MAO catalyst system (run 22).

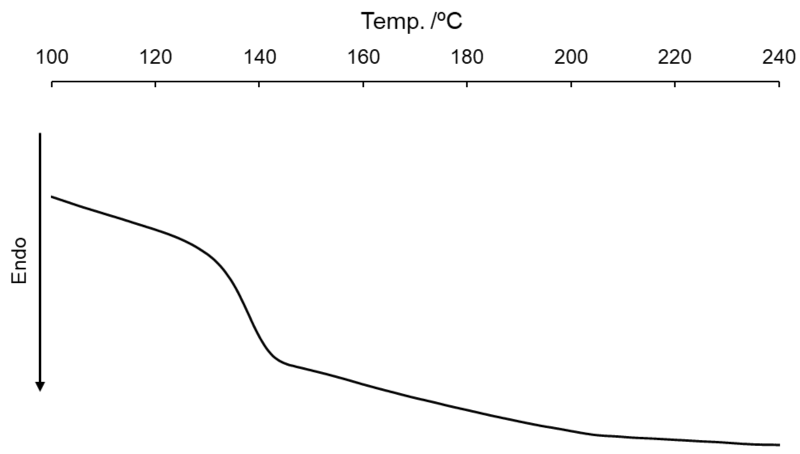

Figure S31. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) – MAO catalyst system (run 24).

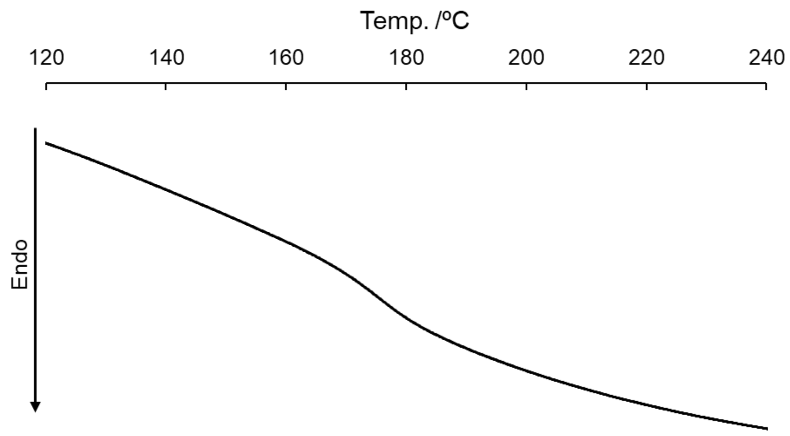

Figure S32. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) – MAO catalyst system (run 26).

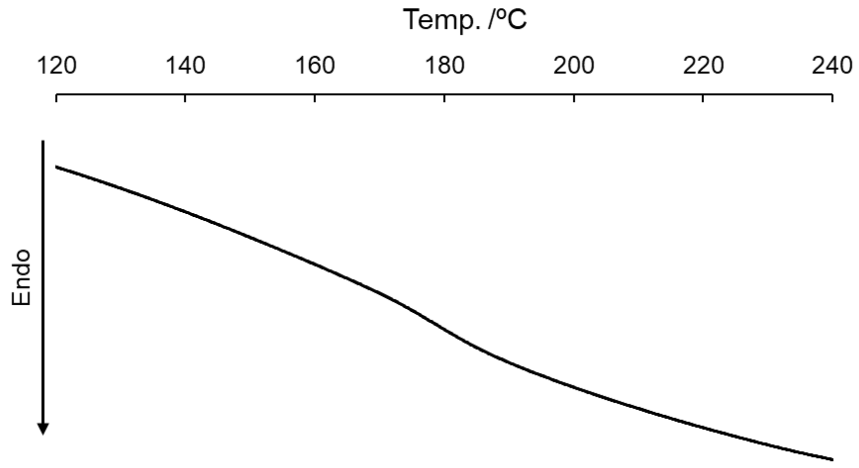

Figure S33. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) – MAO catalyst system (run 27).

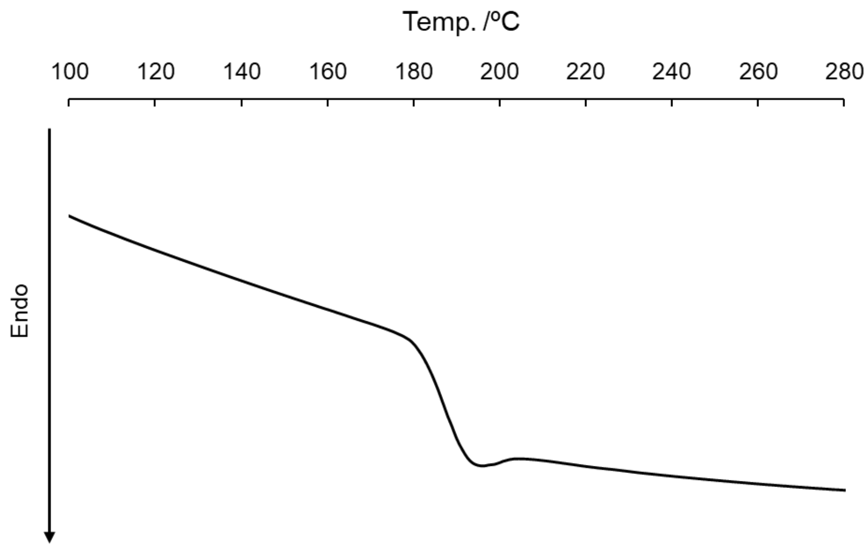

Figure S34. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) – MAO catalyst system (run 28).

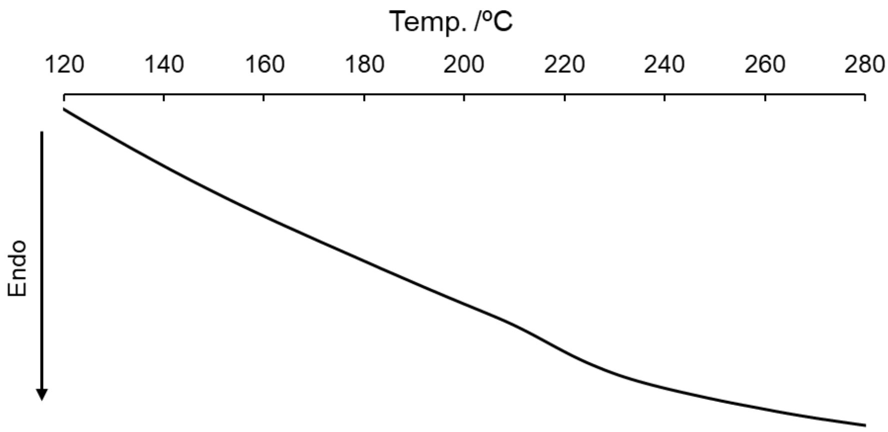

Figure S35. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) – MAO catalyst system (run 29).

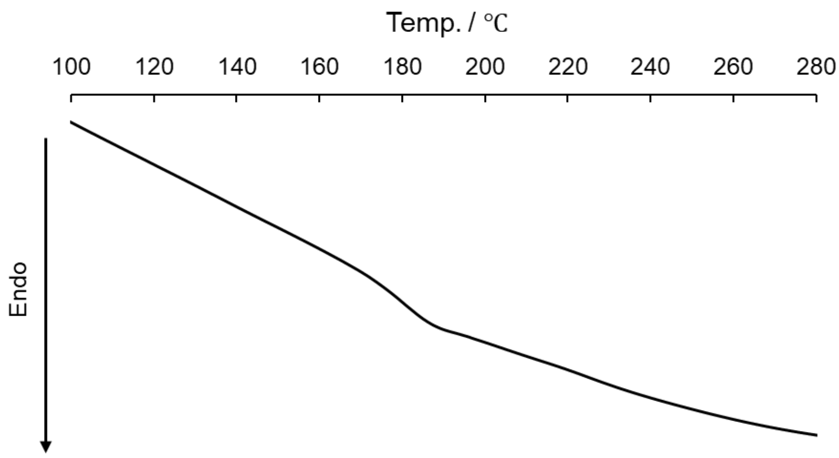

Figure S36. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**) – MAO catalyst system (run 37).

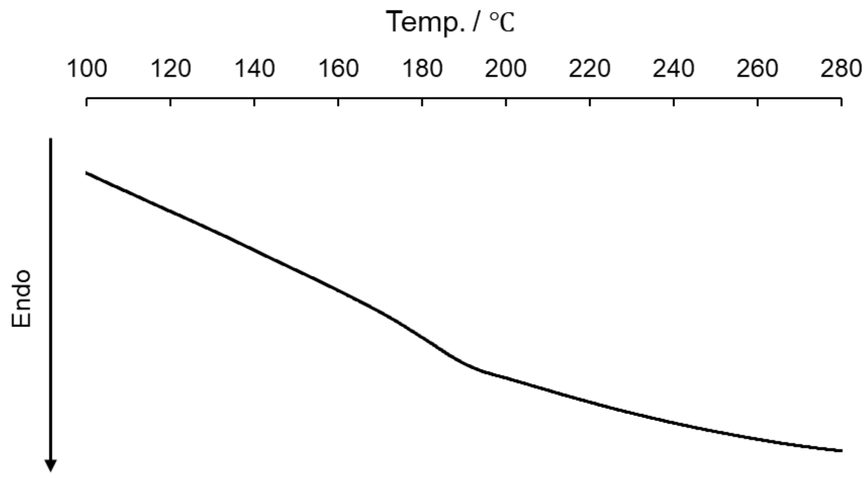

Figure S37. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**) – MAO catalyst system (run 38).

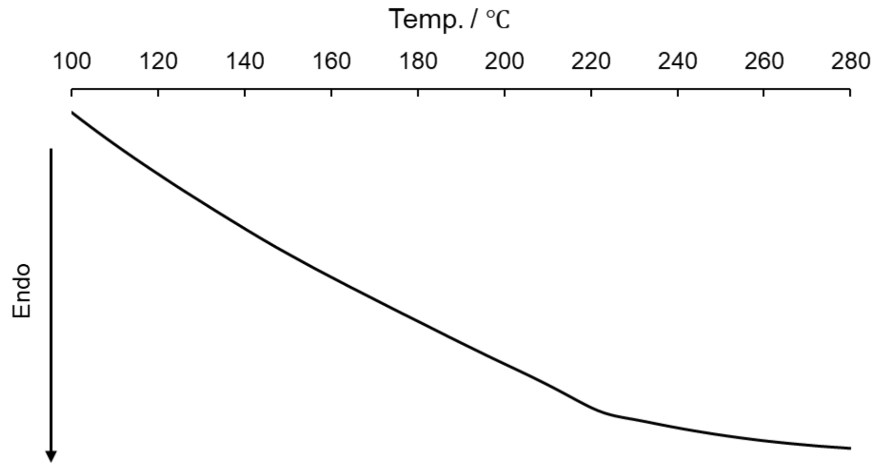

Figure S38. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**) – MAO catalyst system (run 39).

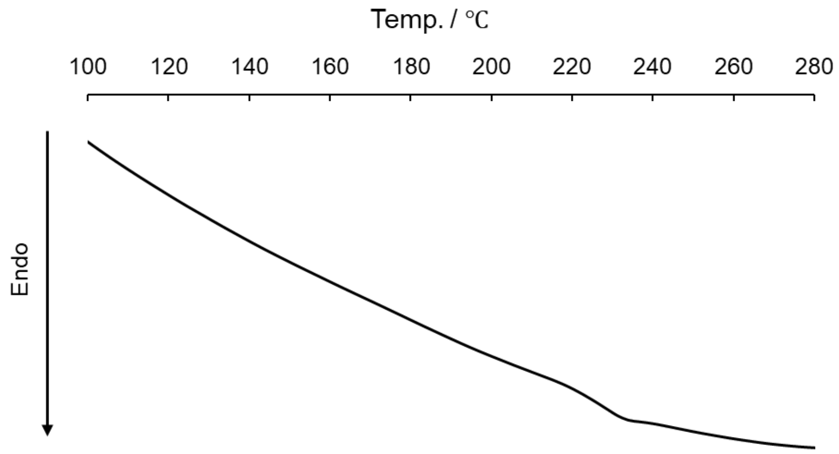

Figure S39. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**) – MAO catalyst system (run 40).

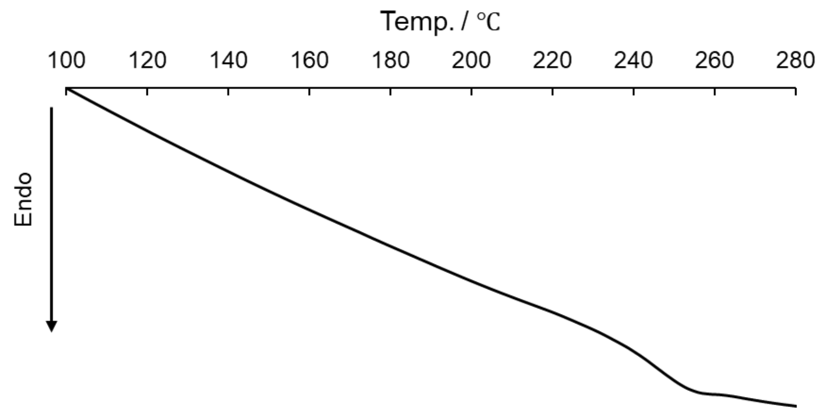

Figure S40. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**) – MAO catalyst system (run 41).

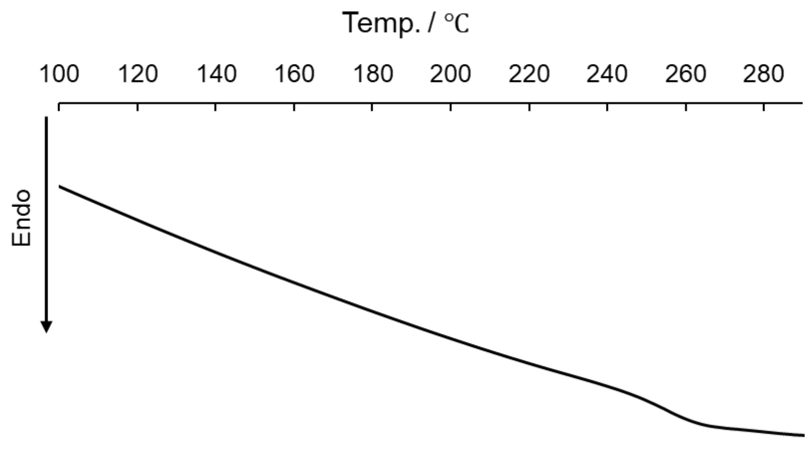

Figure S41. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**2**) – MAO catalyst system (run 42).

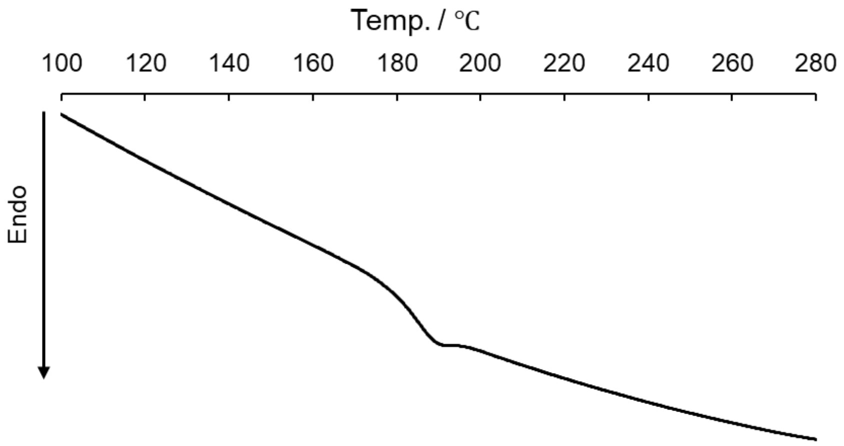

Figure S42. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) – MAO catalyst system (run 43).

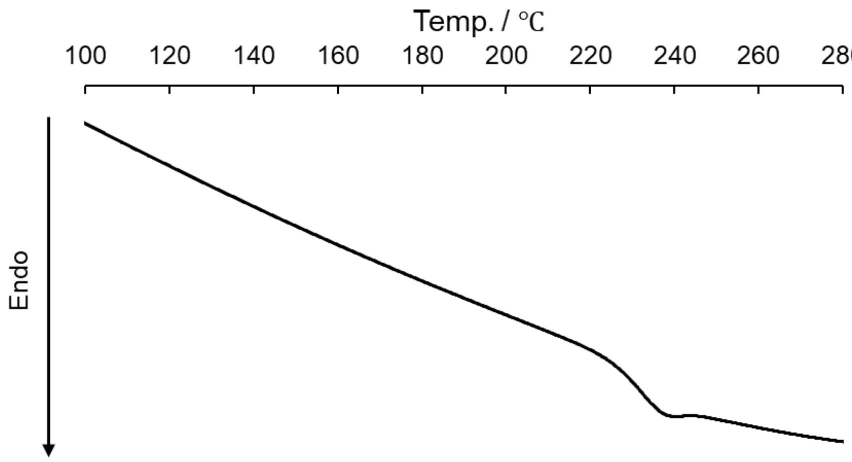

Figure S43. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) – MAO catalyst system (run 45).

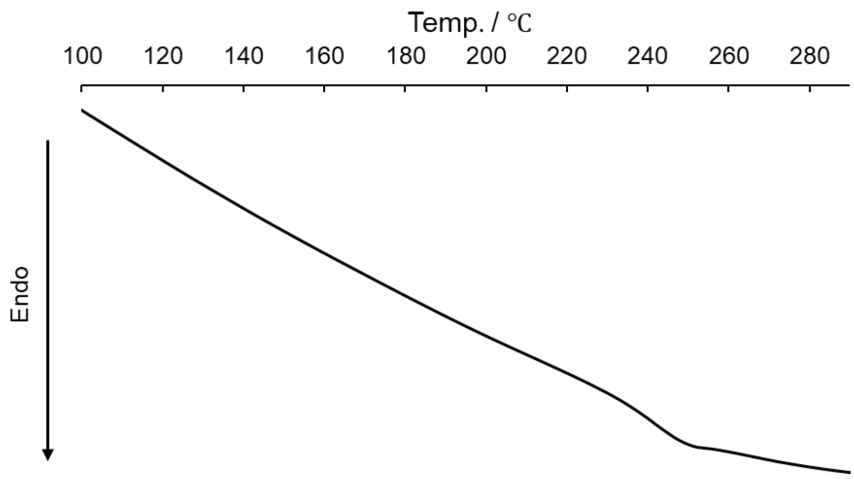

Figure S44. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) – MAO catalyst system (run 46).

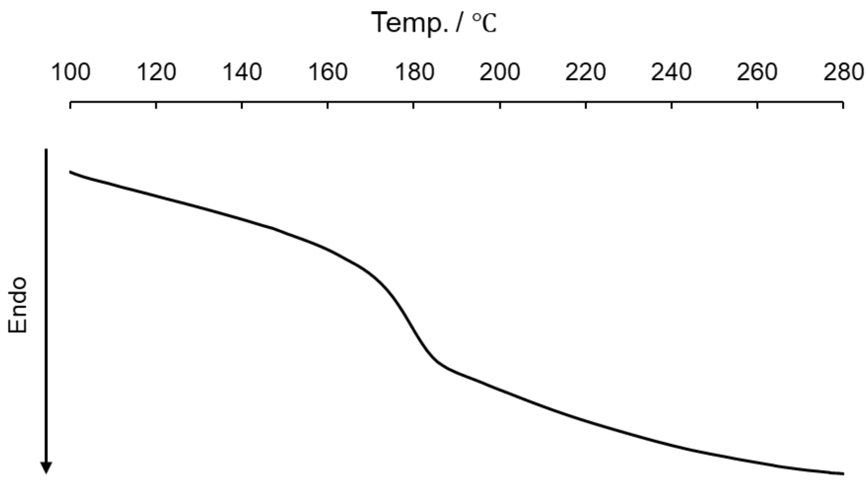

Figure S45. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) – MAO catalyst system (run 49).

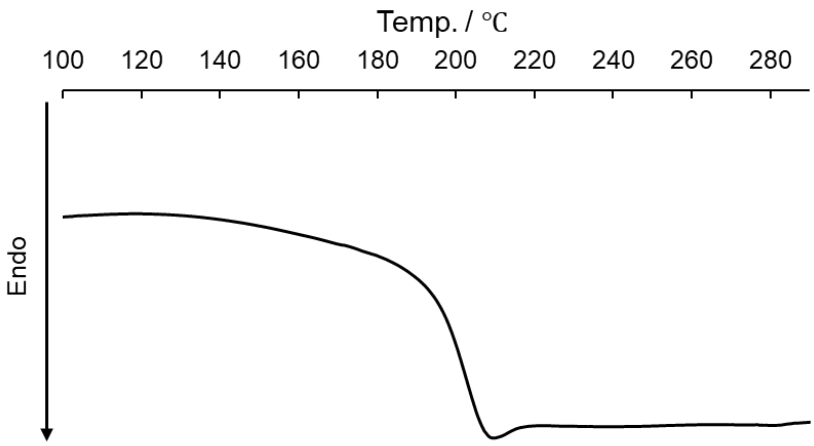

Figure S46. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) – MAO catalyst system (run 50).

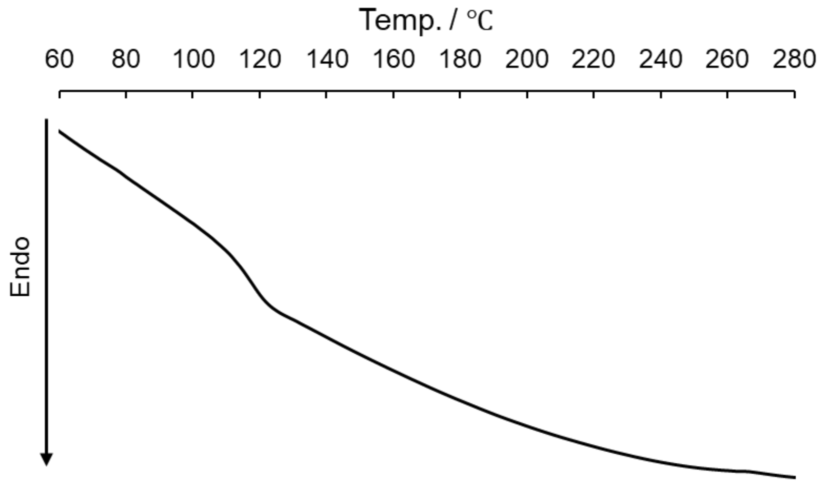

Figure S47. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Et_3SiC_5H_4)TiCl_2(N=C^tBu_2)$ (**3**) – MAO catalyst system (run 51).

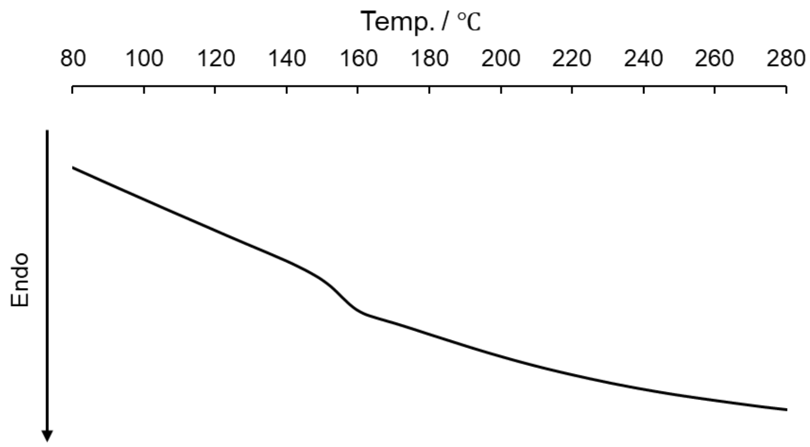

Figure S48. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Et_3SiC_5H_4)TiCl_2(N=C^tBu_2)$ (**3**) – MAO catalyst system (run 51).

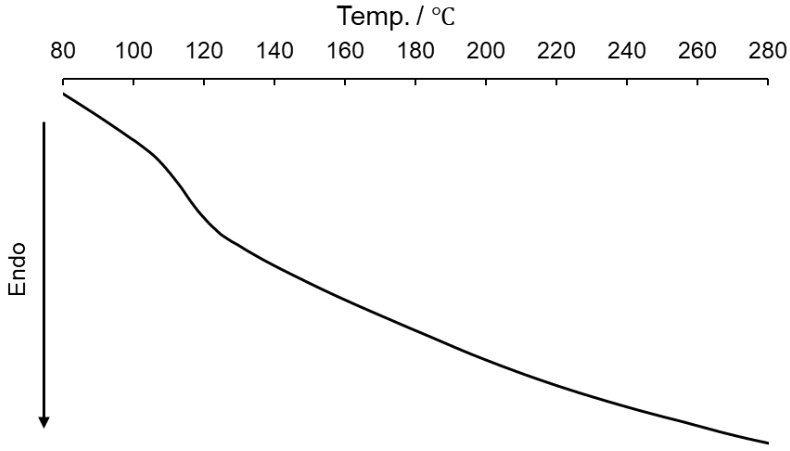

Figure S49. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) – MAO catalyst system (run 53).

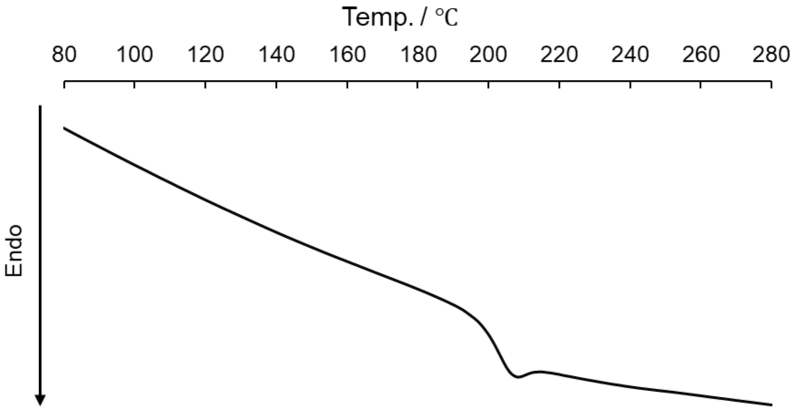

Figure S50. DSC thermogram of poly(ethylene-*co*-tetracyclododecene) prepared by $(Et_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**) – MAO catalyst system (run 54).

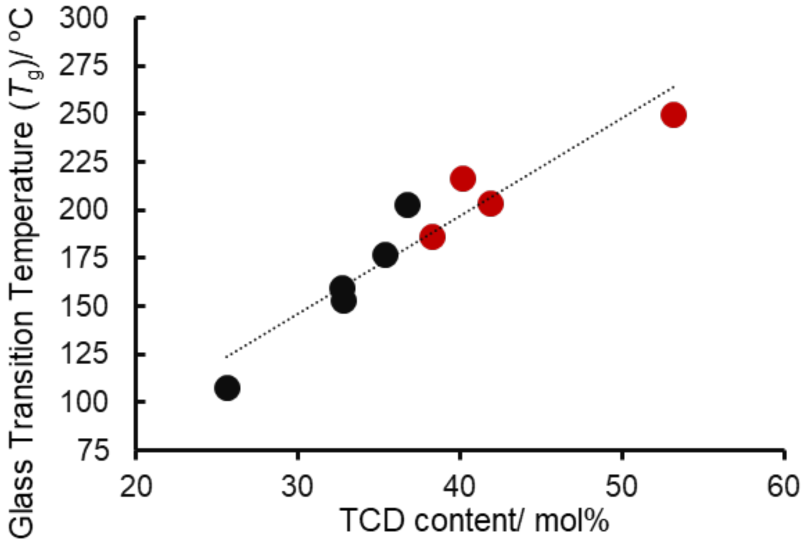

Figure S51. Plots of glass transition temperature (T_g) vs TCD (tetracyclododecene) contents. Data marked in ● are cited in this research and data marked in ● are cited from reference (W. Apisuk, A. G. Trambitas, B. Kitiyanan, M. Tamm and K. Nomura, *J. Polym. Sci. Part A: Polym. Chem.*, 2013, **51**, 2575.).