Electronic Supplementary Information for

Ethylene Polymerization and Ethylene/Norbornene Copolymerization by Aryloxo-Modified Vanadium(V) Complexes Containing 2,6-Difluoro-, Dichloro-phenylimido Complexes

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[†]N. Diteepeng and X.-Y, Tang: equal contribution as the first author

1. Selected ^{13}C NMR spectra of poly(ethylene-*co*-norbornene)s

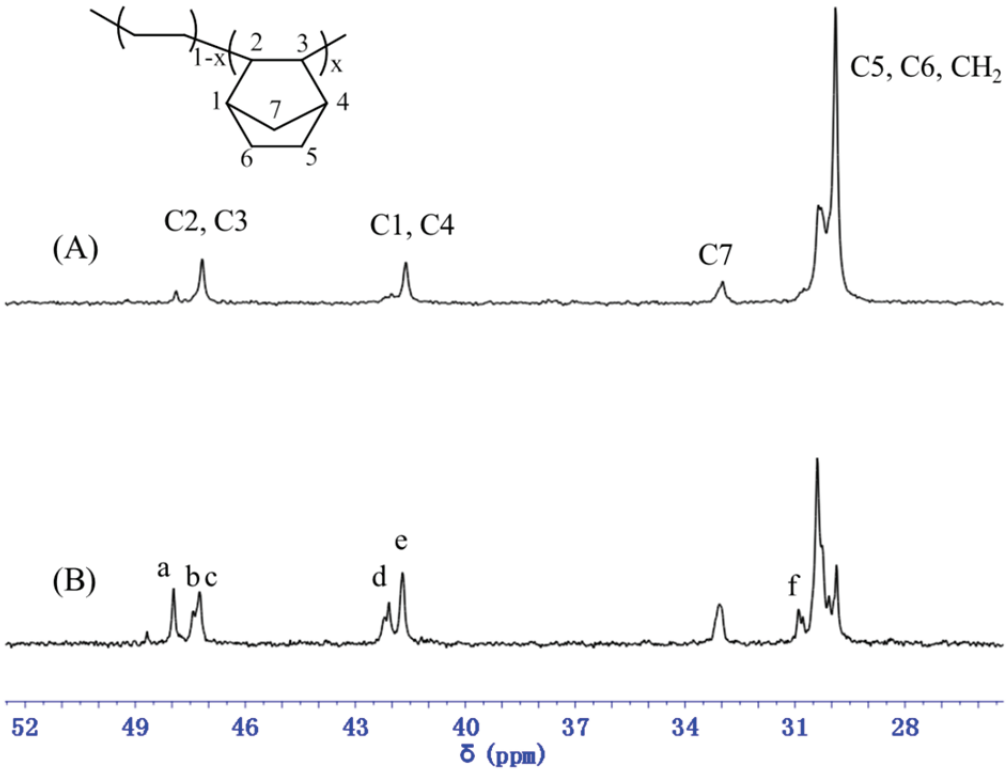

Figure S1-1. ^{13}C NMR spectrum of poly(ethylene-*co*-norbornene) (in 1,2-dichlorobenzene-d_4 at 120 ºC) prepared by (A) VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**)-MAO catalyst system (NBE 9.6 mol%, ethylene 8 atm, NBE 0.5 M, run 44, Table 4) and (B) VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**1b**)-MAO catalyst system (NBE 30.1 mol%, ethylene 8 atm, NBE 4.0 M, run 66, Table 5). [a: alternative isotactic, b: alternative syndiotactic, c: isolated, d: alternative isotactic, e: alternative syndiotactic and + isolated, f: alternative isotactic]

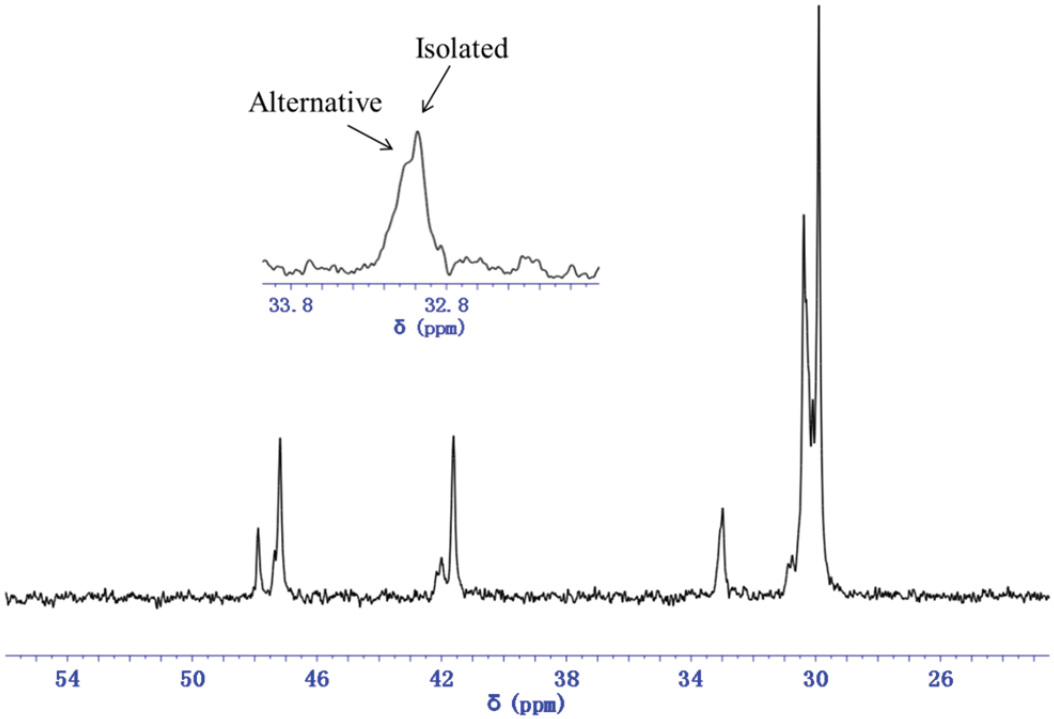

Figure S1-2. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**) - MAO catalyst system (ethylene 8 atm, NBE 1.0 M, run 45, Table 4).

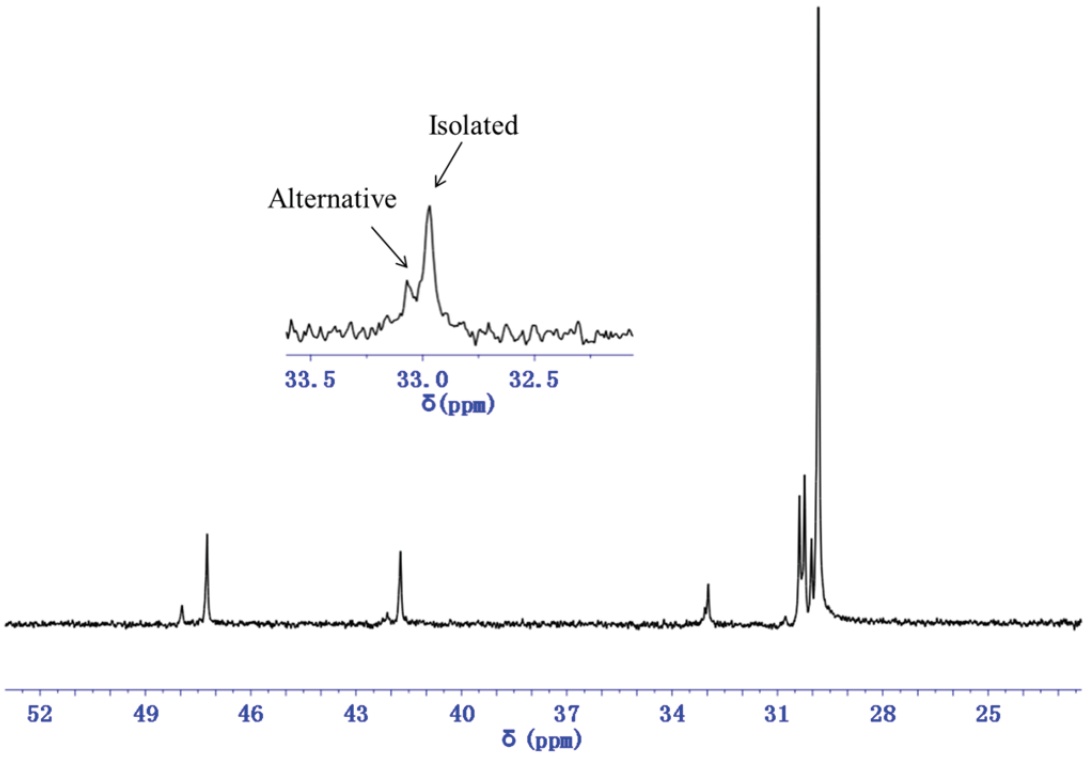

Figure S1-3. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**1b**) - MAO catalyst system (ethylene 8 atm, NBE 0.5 M, run 46, Table 4).

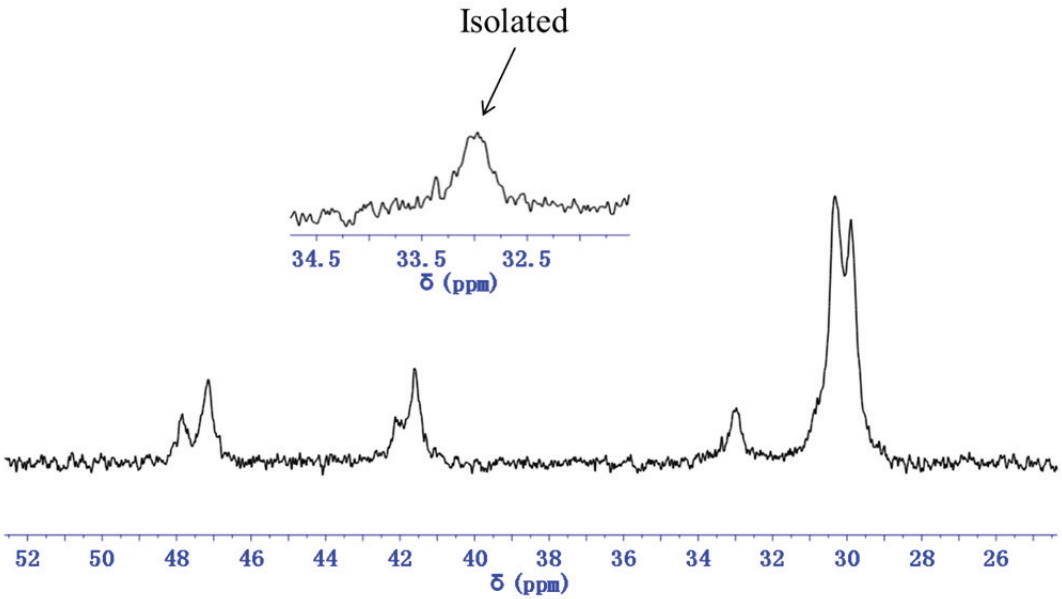

Figure S1-4. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by $VCl_2(N\text{-}2,6\text{-}F_2C_6H_3)(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**2a**) - MAO catalyst system (ethylene 8 atm, NBE 0.5 M, run 48, Table 4).

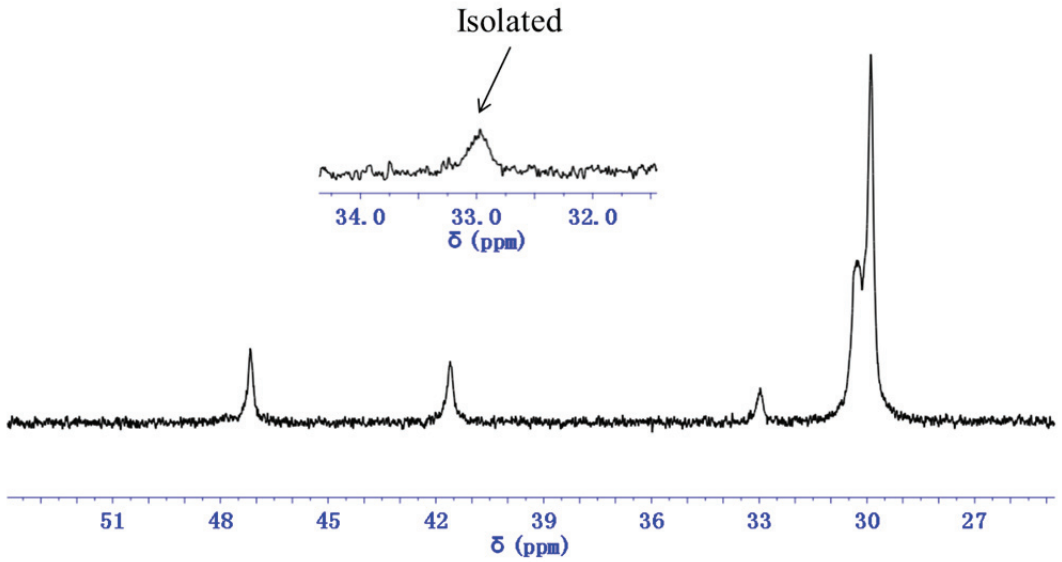

Figure S1-5. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by $VCl_2(N\text{-}2,6\text{-}Cl_2C_6H_3)(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**1a**) – Et_2AlCl catalyst system (ethylene 8 atm, NBE 0.5 M, run 54, Table 4).

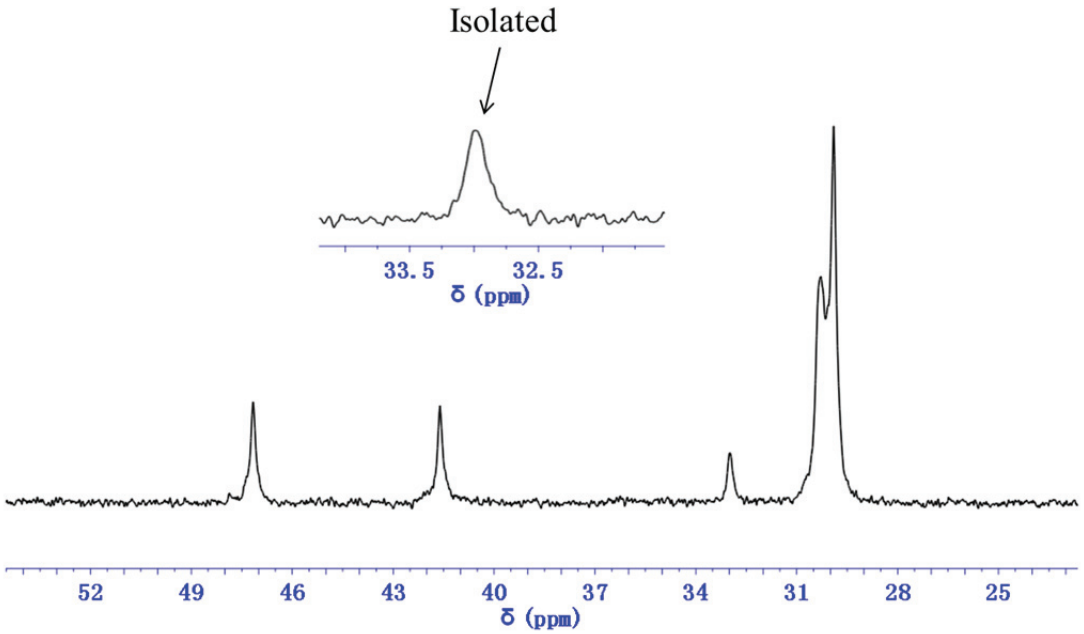

Figure S1-6. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**) – Et_2AlCl catalyst system (ethylene 8 atm, NBE 1.0 M, run 55, Table 4).

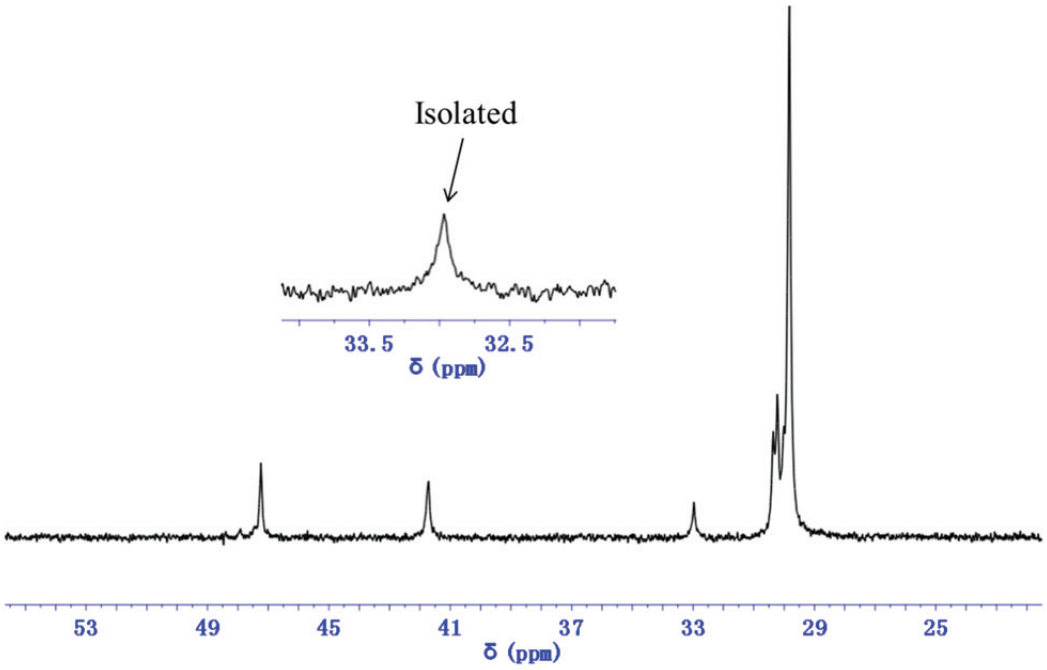

Figure S1-7. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**1b**) – Et_2AlCl catalyst system (ethylene 8 atm, NBE 0.5 M, run 56, Table 4).

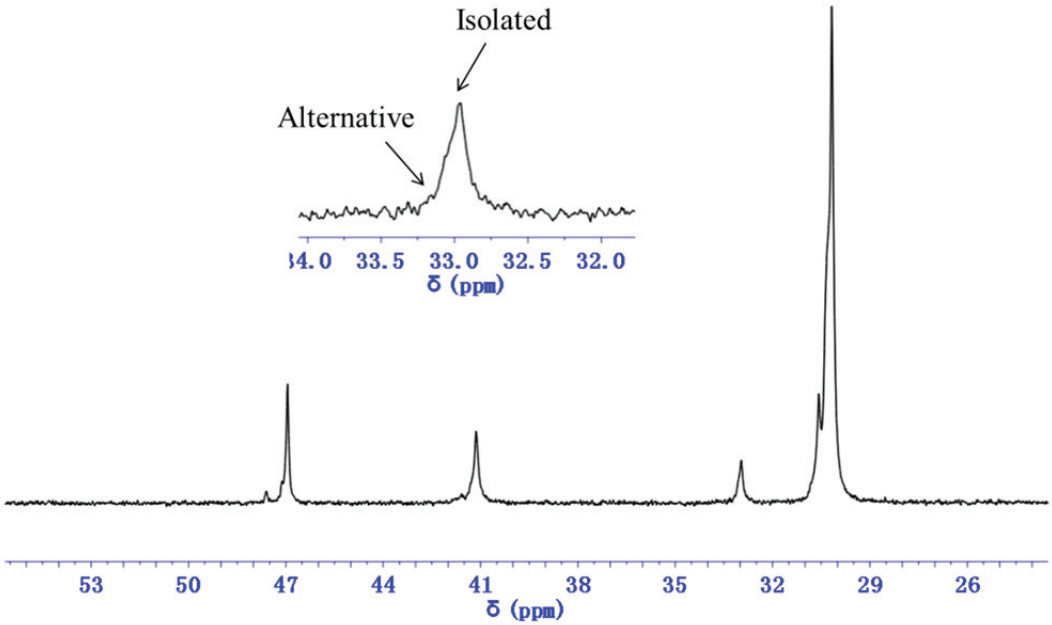

Figure S1-8. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by $VCl_2(N\text{-}2,6\text{-}F_2C_6H_3)(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**2a**) – Et_2AlCl catalyst system (ethylene 8 atm, NBE 0.5 M, run 58, Table 4).

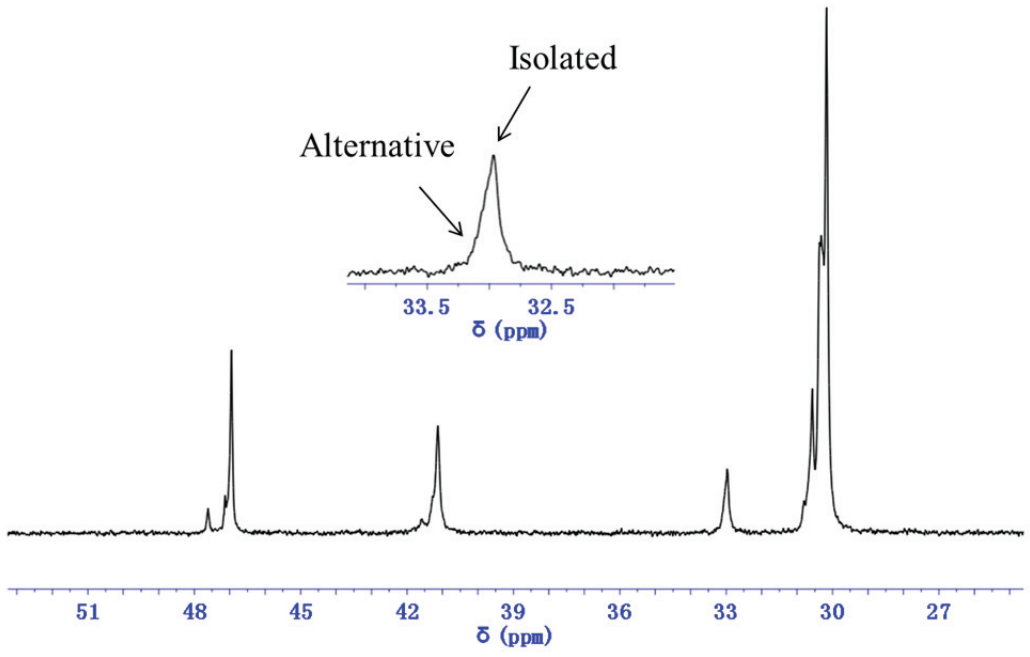

Figure S1-9. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by $VCl_2(N\text{-}2,6\text{-}F_2C_6H_3)(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**2a**) – Et_2AlCl catalyst system (ethylene 8 atm, NBE 1.0 M, run 59, Table 4).

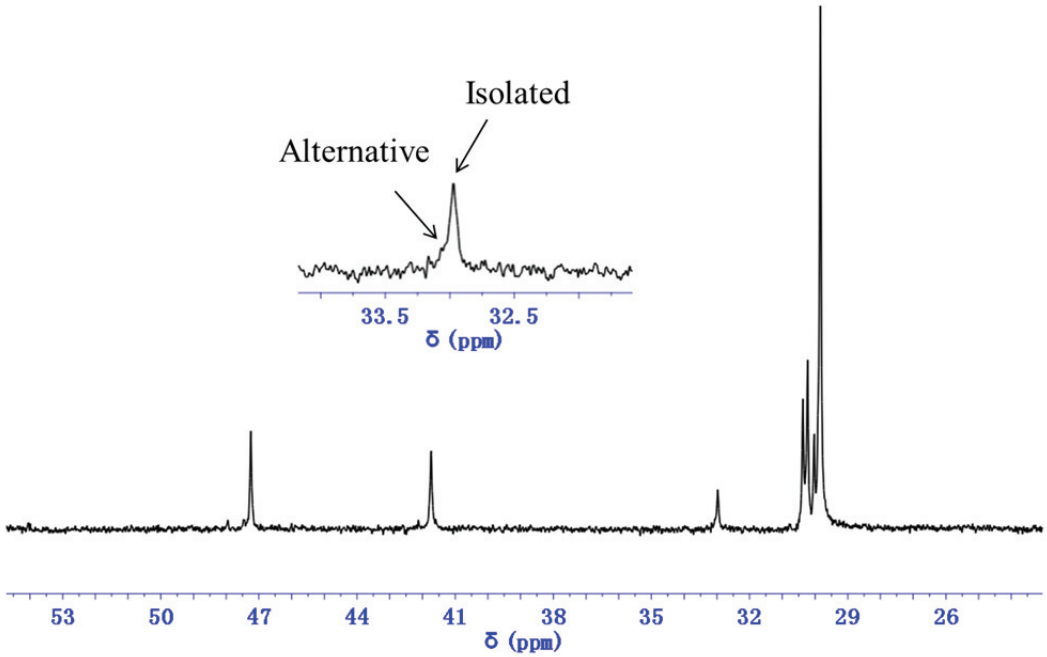

Figure S1-10. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by VCl_2(N-2,6-$F_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**2b**) – Et_2AlCl catalyst system (ethylene 8 atm, NBE 0.5 M, run 60, Table 4).

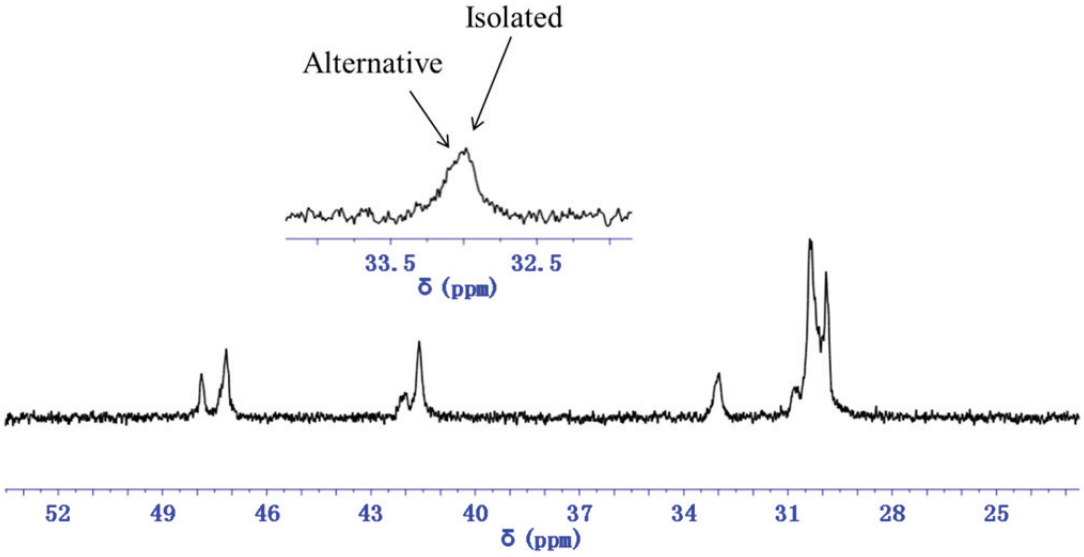

Figure S1-11. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**1b**) – MAO catalyst system (ethylene 8 atm, NBE 2.0 M, run 64, Table 5).

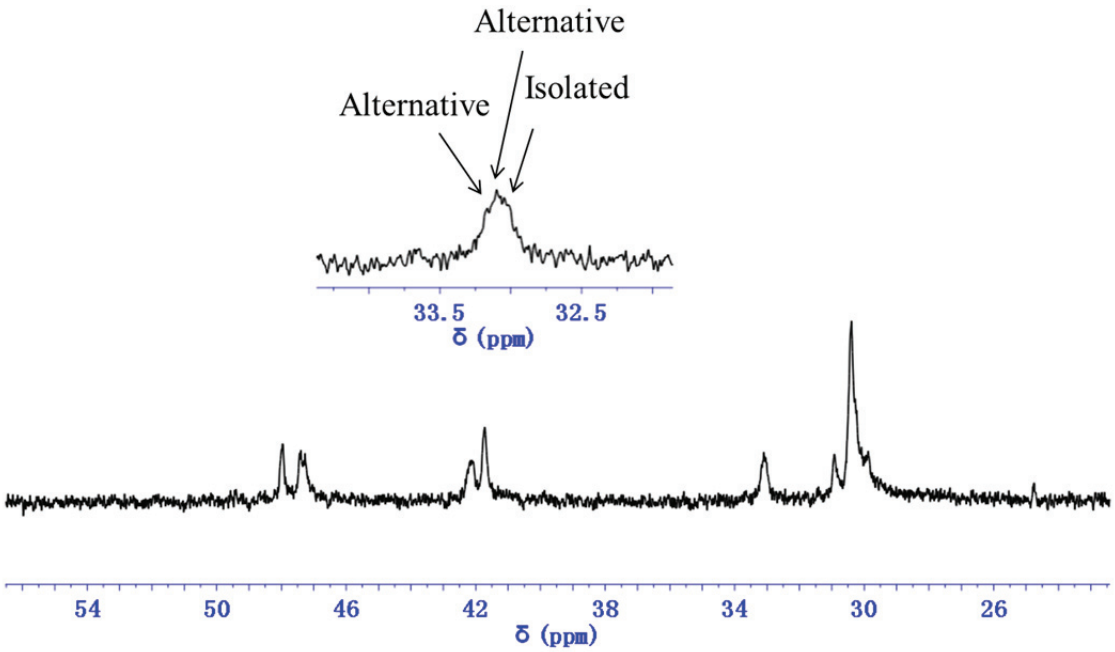

Figure S1-12. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by $VCl_2(N\text{-}2,6\text{-}Cl_2C_6H_3)(O\text{-}2,6\text{-}F_2C_6H_3)$ (**1b**) – MAO catalyst system (ethylene 4 atm, NBE 5.0 M, run 68, Table 5).

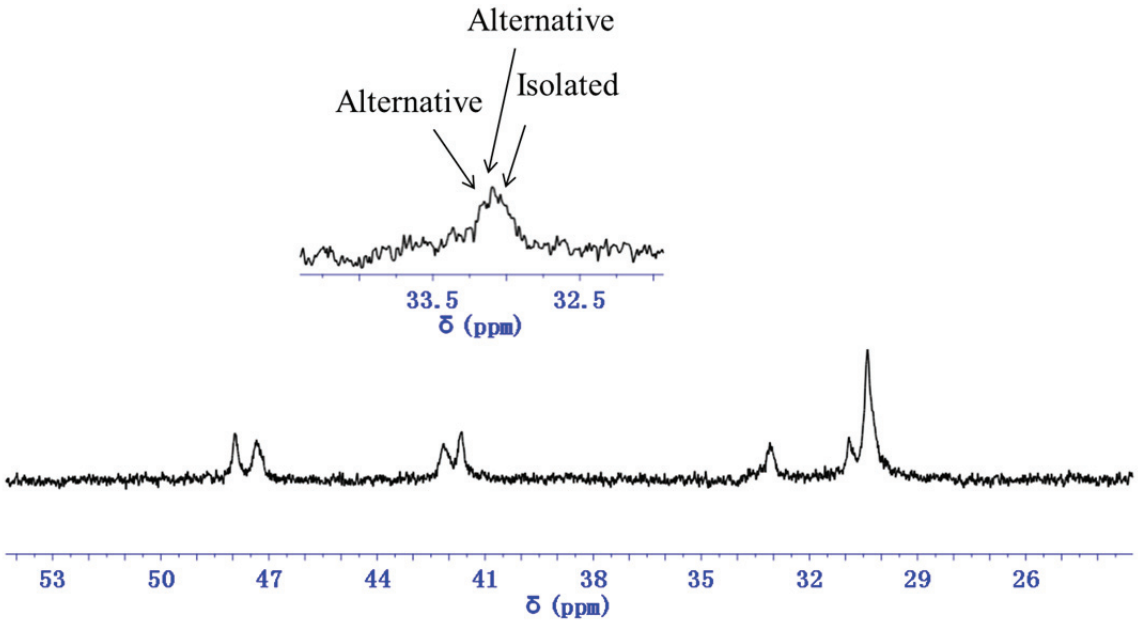

Figure S1-13. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by $VCl_2(N\text{-}2,6\text{-}Cl_2C_6H_3)(O\text{-}2,6\text{-}F_2C_6H_3)$ (**1b**) – MAO catalyst system (ethylene 2 atm, NBE 5.0 M, run 69, Table 5).

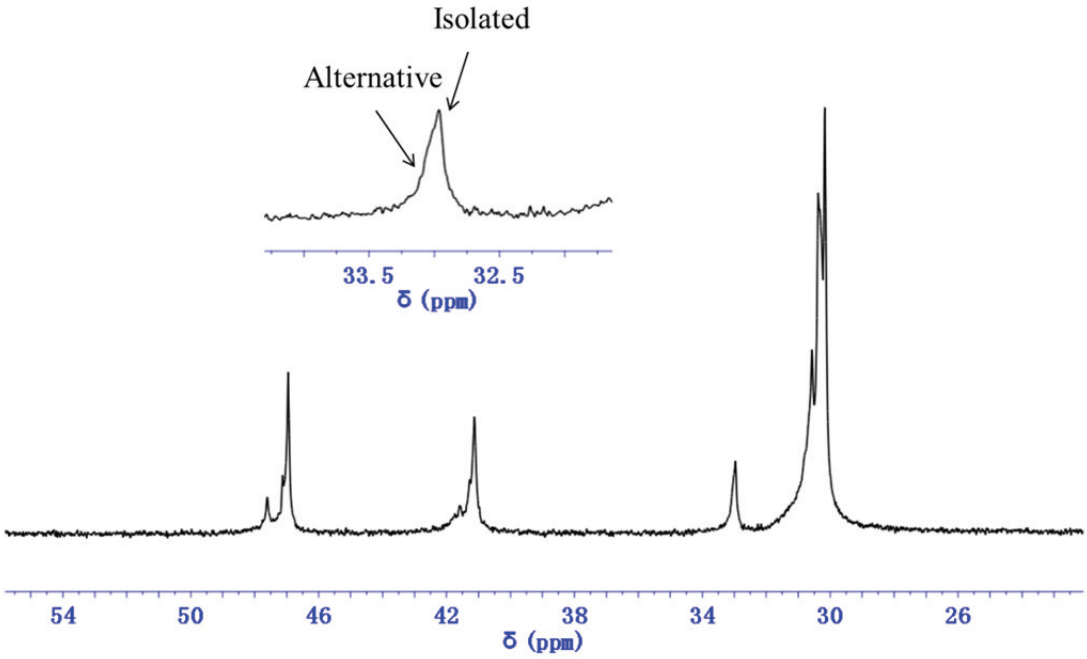

Figure S1-14. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**) – Et_2AlCl catalyst system (ethylene 8 atm, NBE 2.0 M, run 70, Table 5).

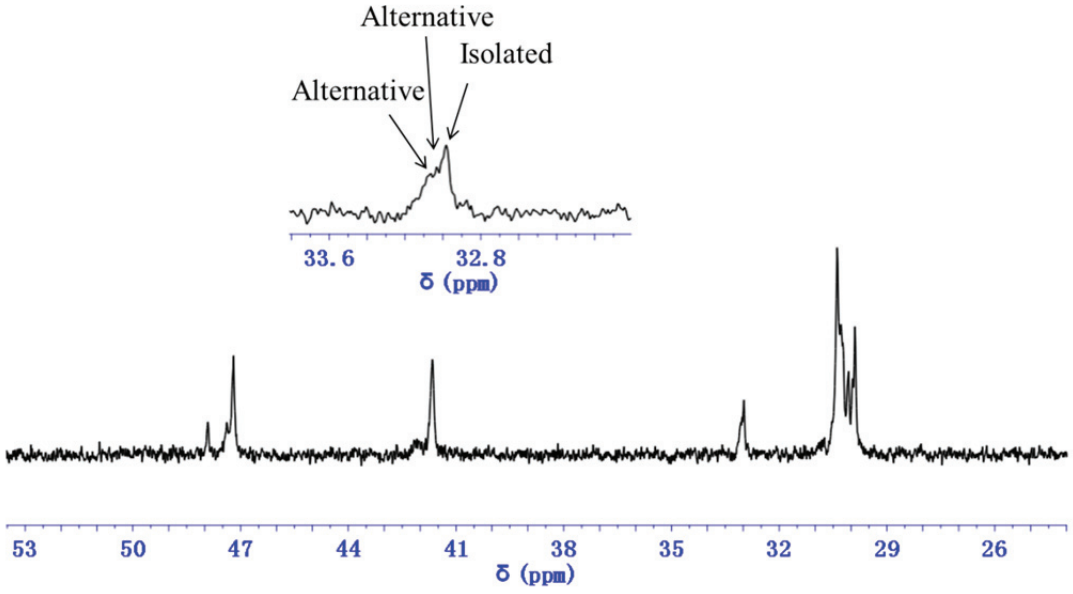

Figure S1-15. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**) – Et_2AlCl catalyst system (ethylene 8 atm, NBE 3.0 M, run 71, Table 5).

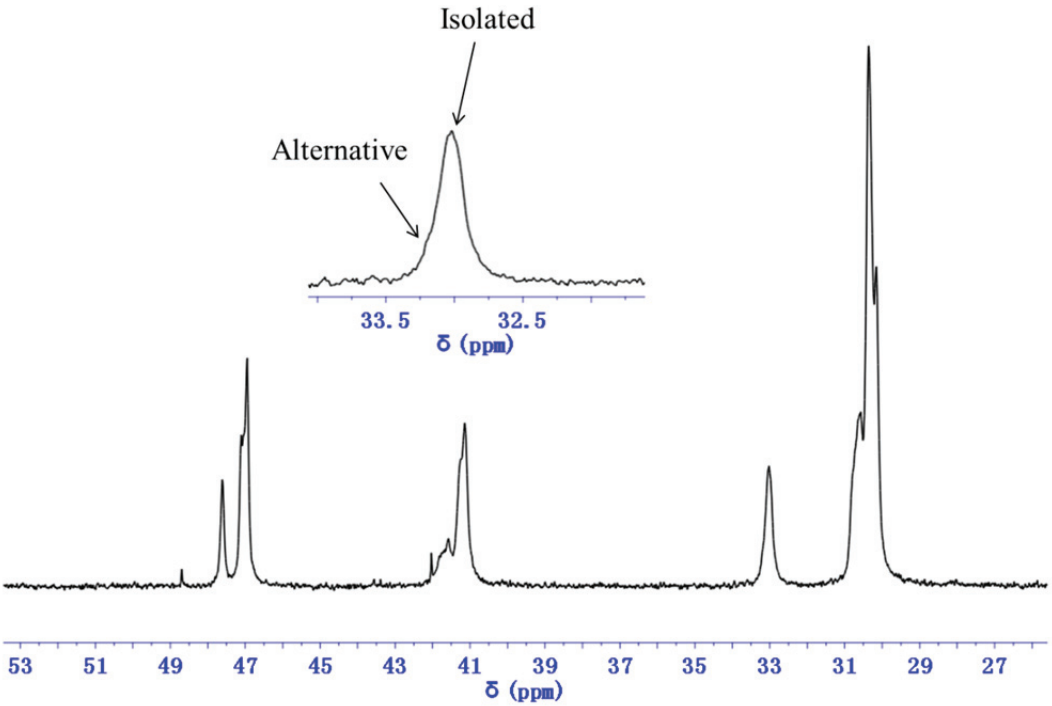

Figure S1-16. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) of poly(ethylene-*co*norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**) – Et_2AlCl catalyst system (ethylene 8 atm, NBE 4.0 M, run 72, Table 5).

2. Selected DSC thermograms spectra of poly(ethylene-*co*-norbornene)s

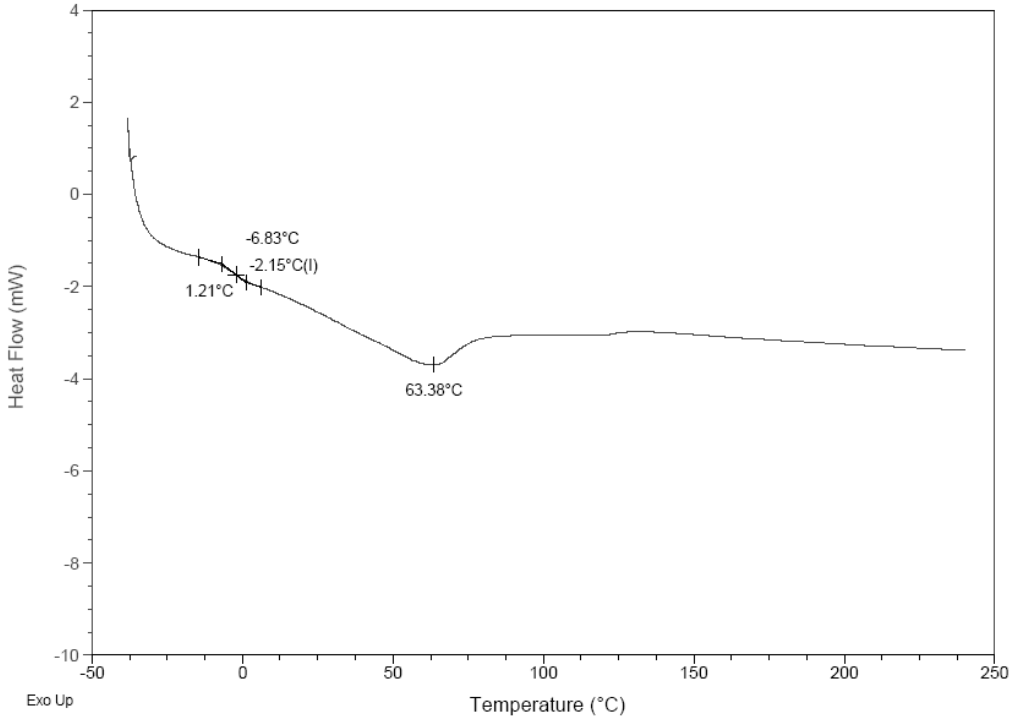

Figure S2-1. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**)-MAO catalyst system (NBE 9.6 mol%, ethylene 8 atm, NBE conc. 0.5 M, run 44, Table 4). (The samples were heated at a rate of 20 °C/min and cooled down at a rate of 20 °C/min)

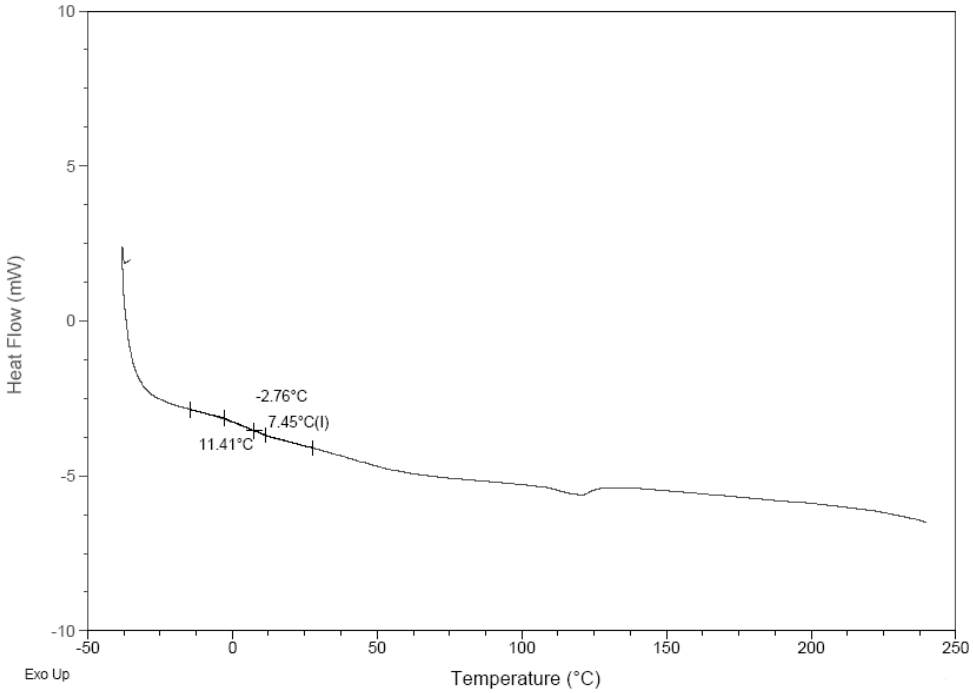

Figure S2-2. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**)-MAO catalyst system (NBE 15.8 mol%, ethylene 8 atm, NBE conc. 1.0 M, run 45, Table 4).

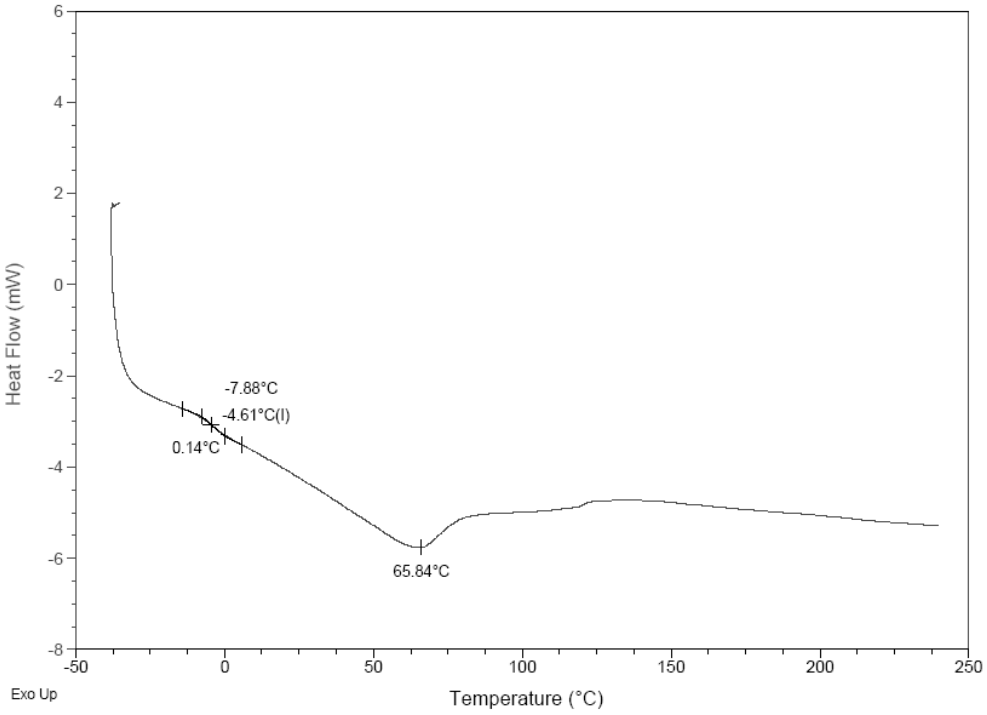

Figure S2-3. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**1b**)-MAO catalyst system (NBE 10.4 mol%, ethylene 8 atm, NBE conc. 0.5 M, run 46, Table 4).

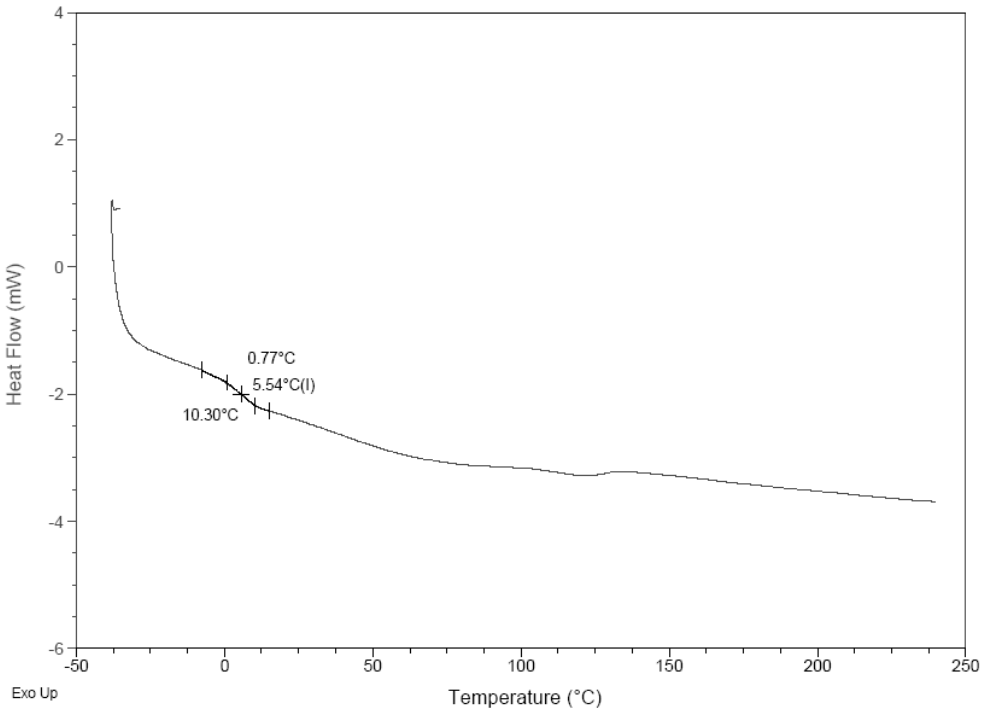

Figure S2-4. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**1b**)-MAO catalyst system (NBE 16.3 mol%, ethylene 8 atm, NBE conc. 1.0 M, run 47, Table 4).

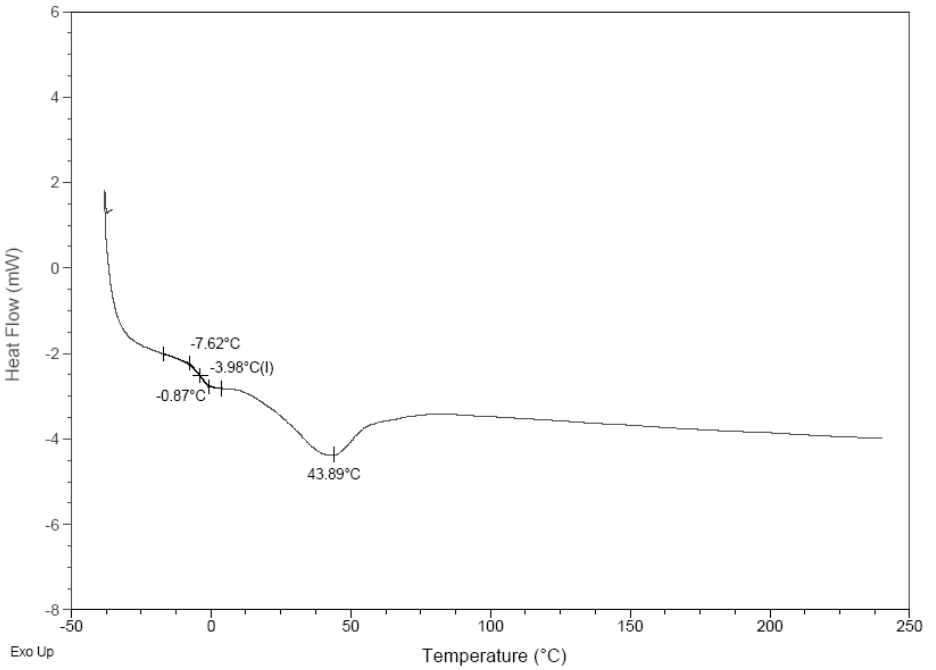

Figure S2-5. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**)-Et_2AlCl catalyst system (NBE 9.4 mol%, ethylene 8 atm, NBE conc. 0.5 M, run 54, Table 4).

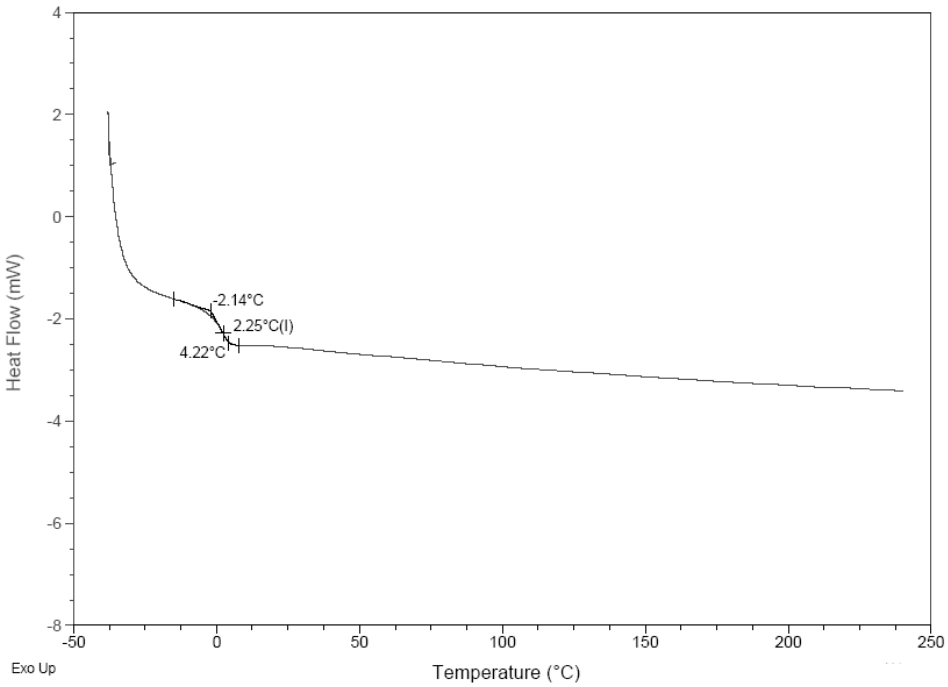

Figure S2-6. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**)-Et_2AlCl catalyst system (NBE 12.1 mol%, ethylene 8 atm, NBE conc. 1.0 M, run 55, Table 4).

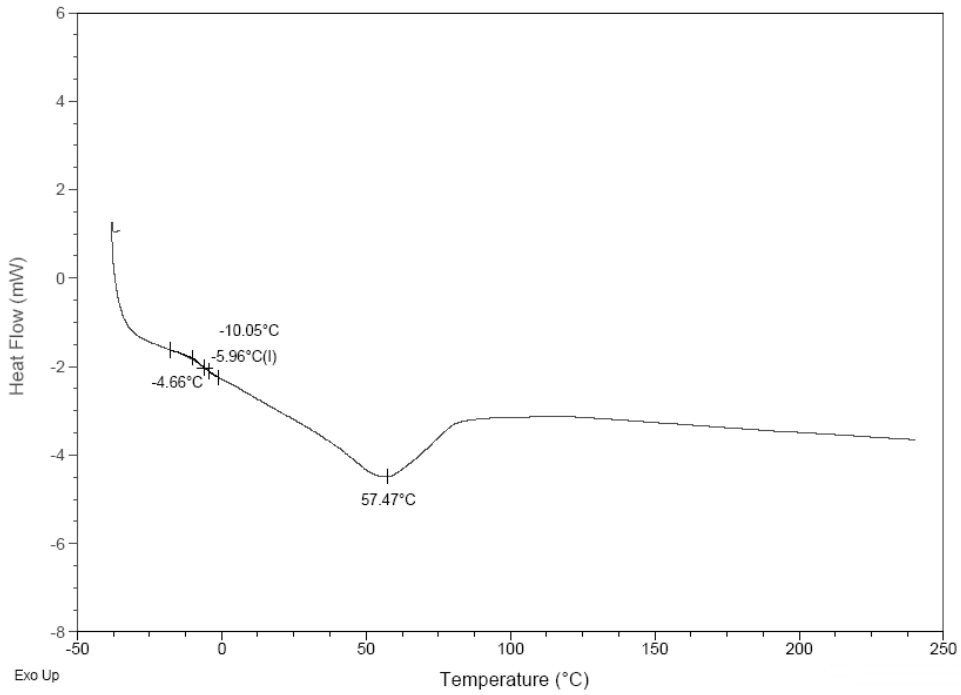

Figure S2-7. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**1b**)-Et_2AlCl catalyst system (NBE 8.0 mol%, ethylene 8 atm, NBE conc. 0.5 M, run 56, Table 4).

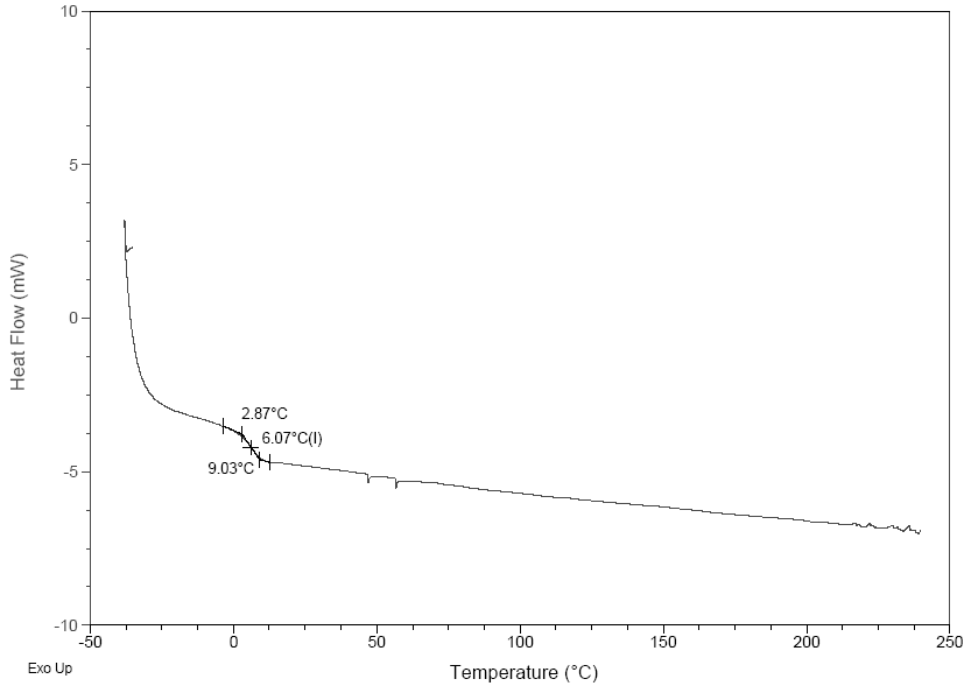

Figure S2-8. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**1b**)-Et_2AlCl catalyst system (NBE 14.2 mol%, ethylene 8 atm, NBE conc. 1.0 M, run 57, Table 4).

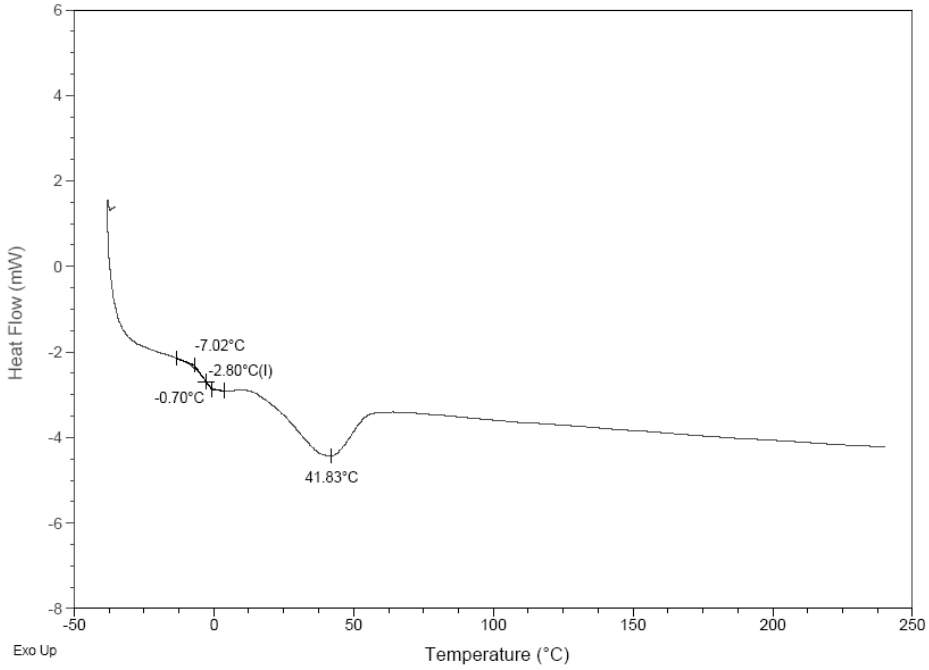

Figure S2-9. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**2a**)-Et_2AlCl catalyst system (NBE 10.0 mol%, ethylene 8 atm, NBE conc. 0.5 M, run 58, Table 4).

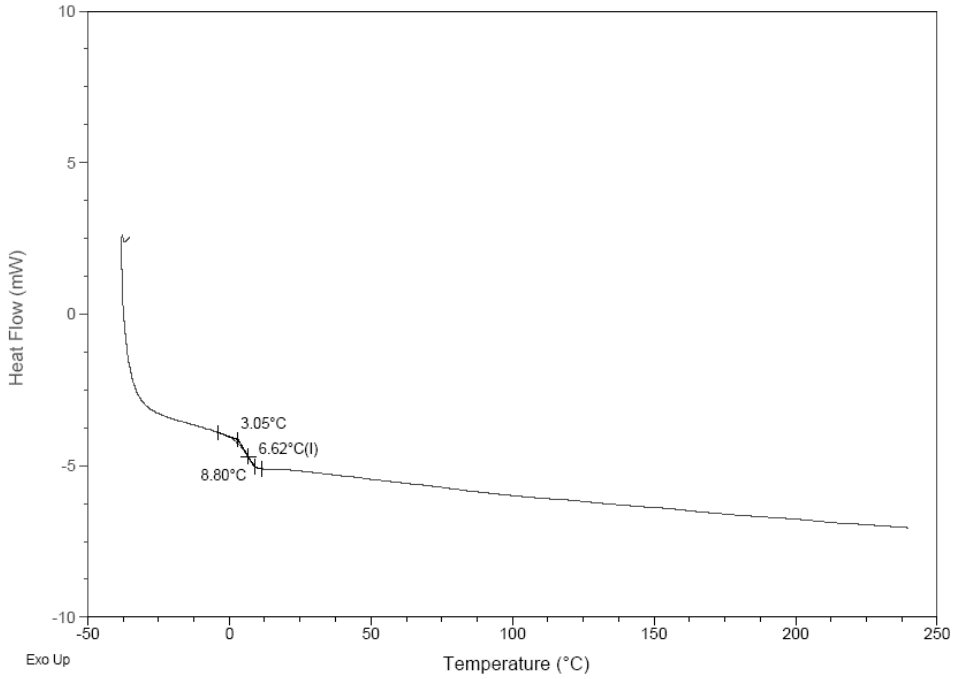

Figure S2-10. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**2a**)-Et_2AlCl catalyst system (NBE 14.3 mol%, ethylene 8 atm, NBE conc. 1.0 M, run 59, Table 4).

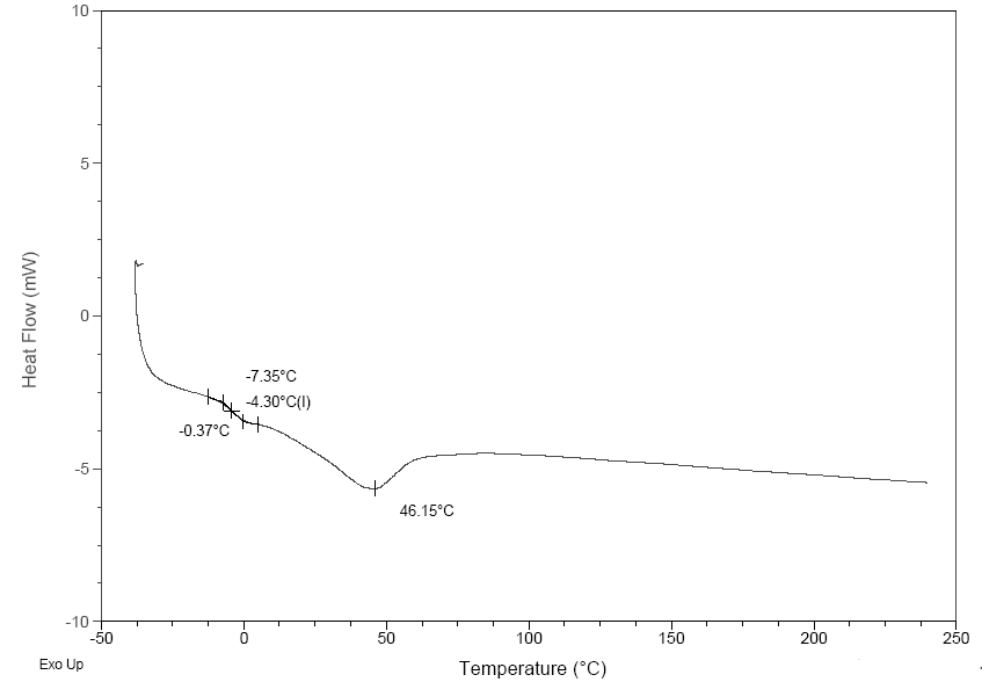

Figure S2-11. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$F_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**2b**)-Et_2AlCl catalyst system (NBE 11.6 mol%, ethylene 8 atm, NBE conc. 0.5 M, run 60, Table 4).

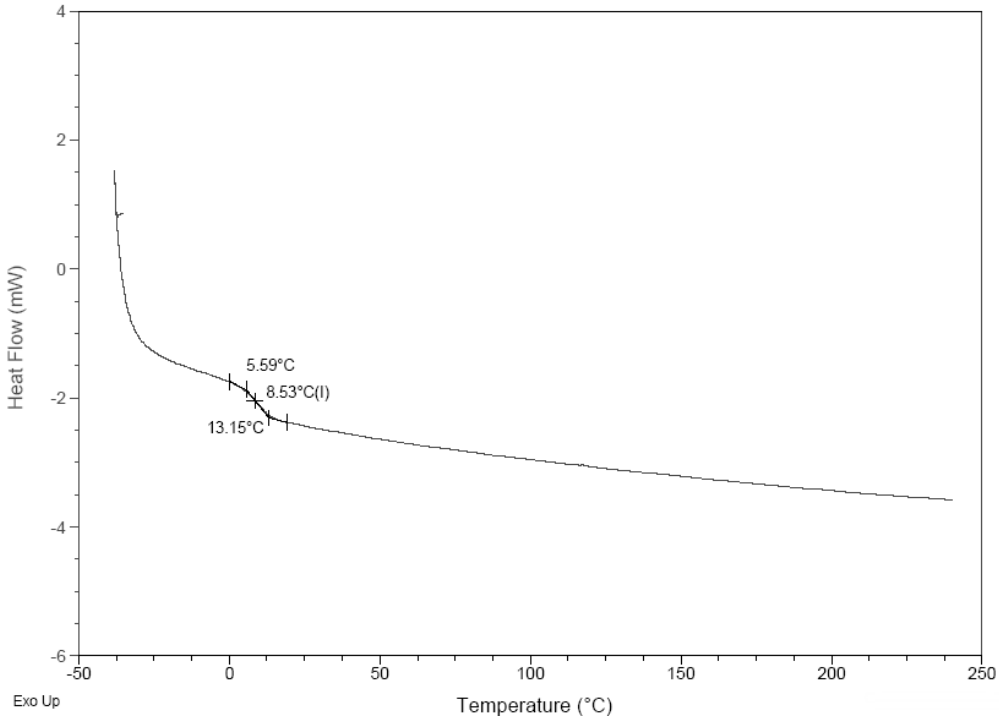

Figure S2-12. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$F_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**2b**)-Et_2AlCl catalyst system (NBE 16.8 mol%, ethylene 8 atm, NBE conc. 1.0 M, run 61, Table 4).

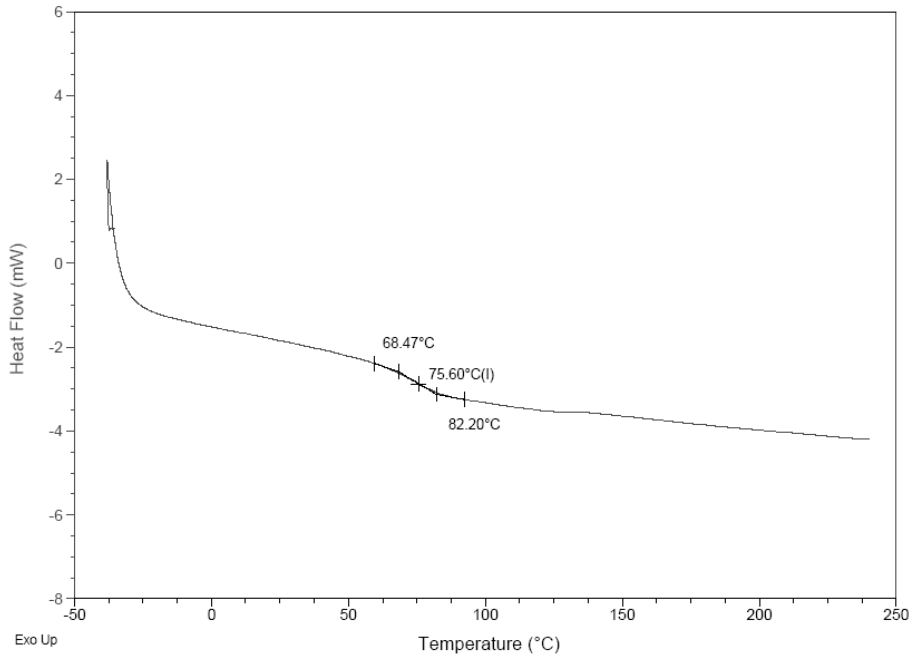

Figure S2-13. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**1b**)-MAO catalyst system (NBE 30.1 mol%, ethylene 8 atm, NBE conc. 4.0 M, run 66, Table 5).

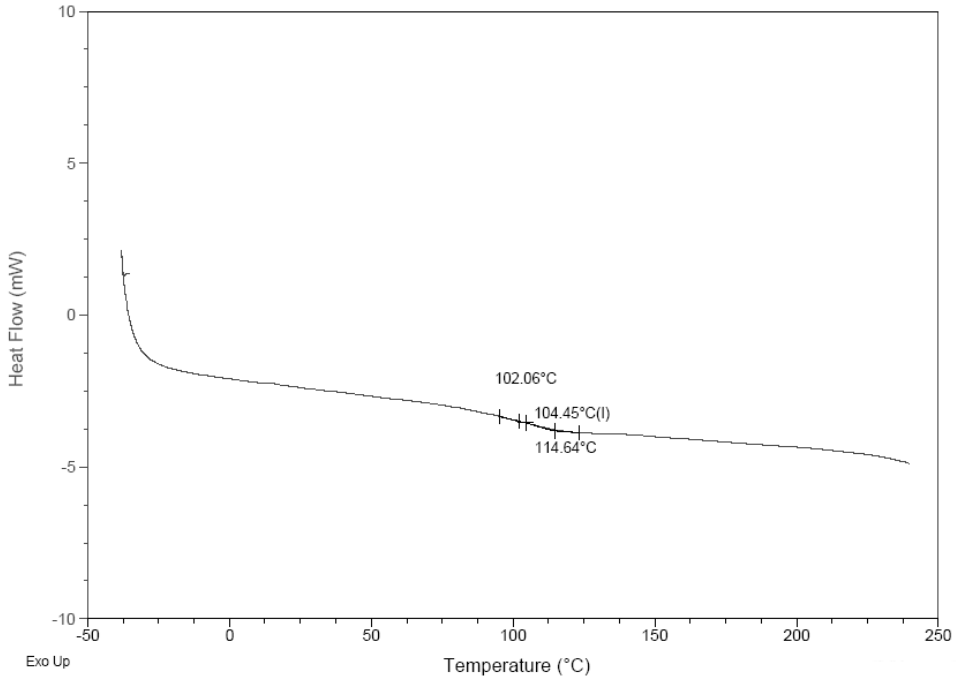

Figure S2-14. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**1b**)-MAO catalyst system (NBE 35.7 mol%, ethylene 4 atm, NBE conc. 5.0 M, run 68, Table 5).

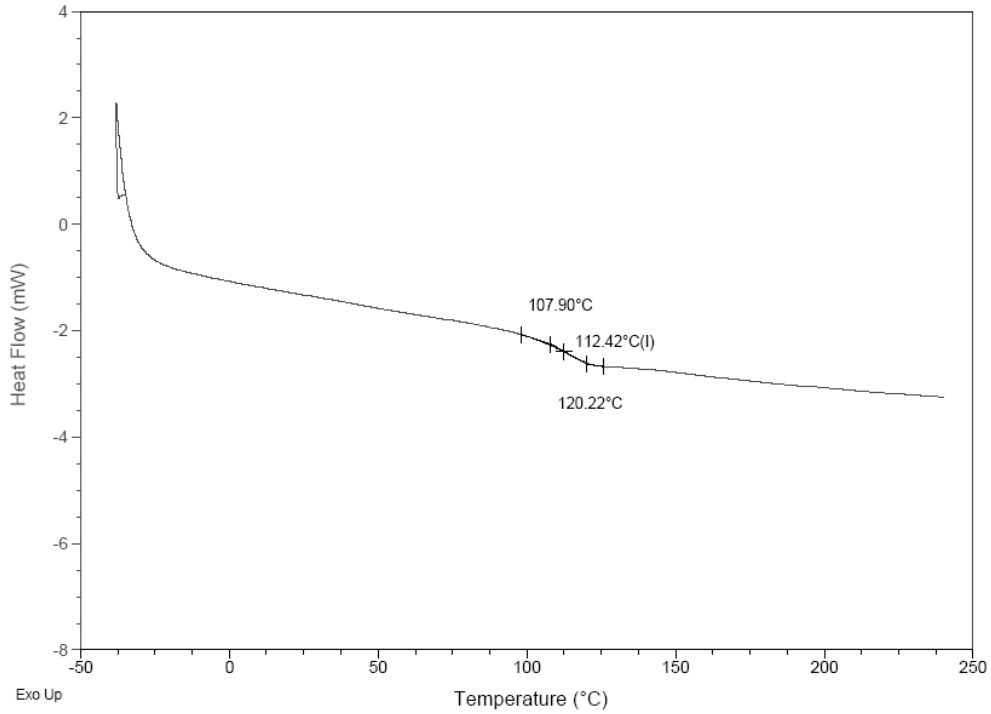

Figure S2-15. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$F_2C_6H_3$) (**1b**)-MAO catalyst system (NBE 41.1 mol%, ethylene 2 atm, NBE conc. 5.0 M, run 69, Table 5).

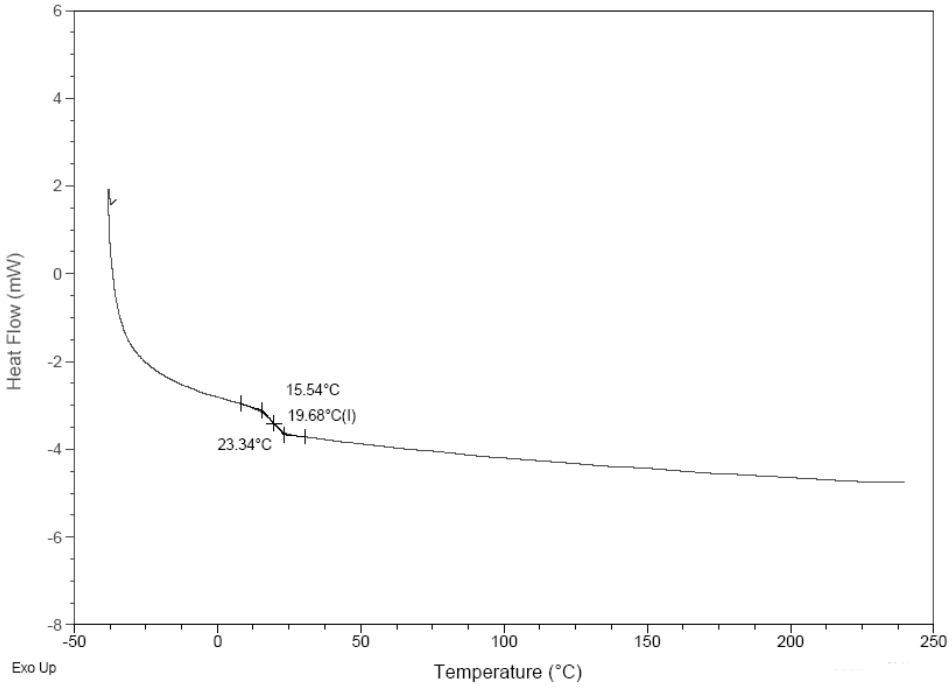

Figure S2-16. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**)-Et_2AlCl catalyst system (NBE 16.4 mol%, ethylene 8 atm, NBE conc. 2.0 M, run 70, Table 5).

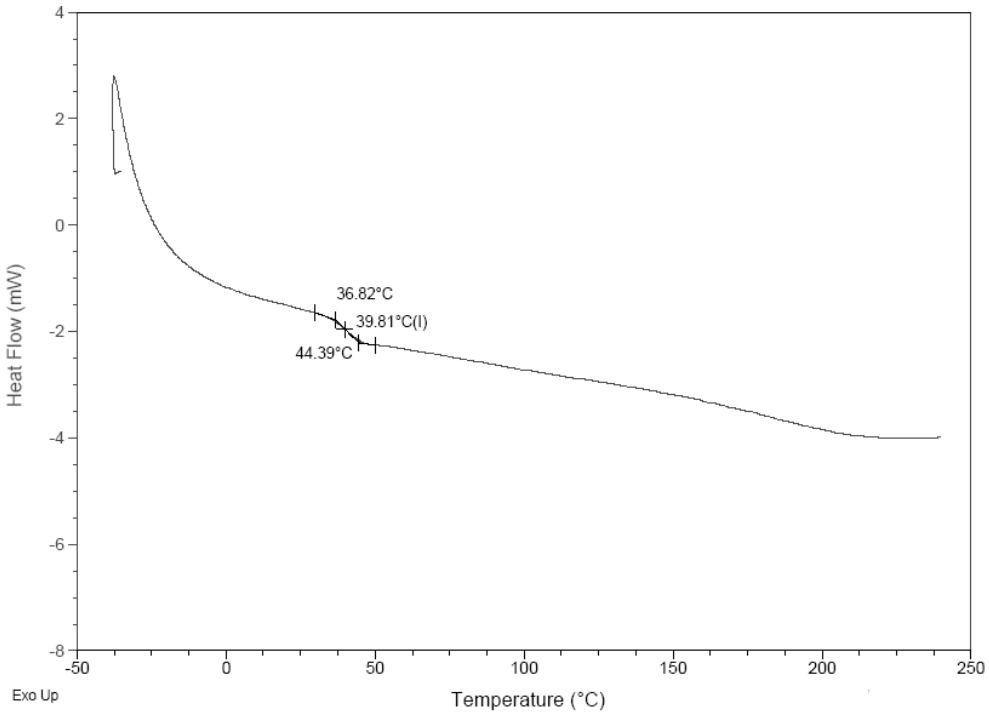

Figure S2-17. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**)-Et_2AlCl catalyst system (NBE 21.2 mol%, ethylene 8 atm, NBE conc. 3.0 M, run 71, Table 5).

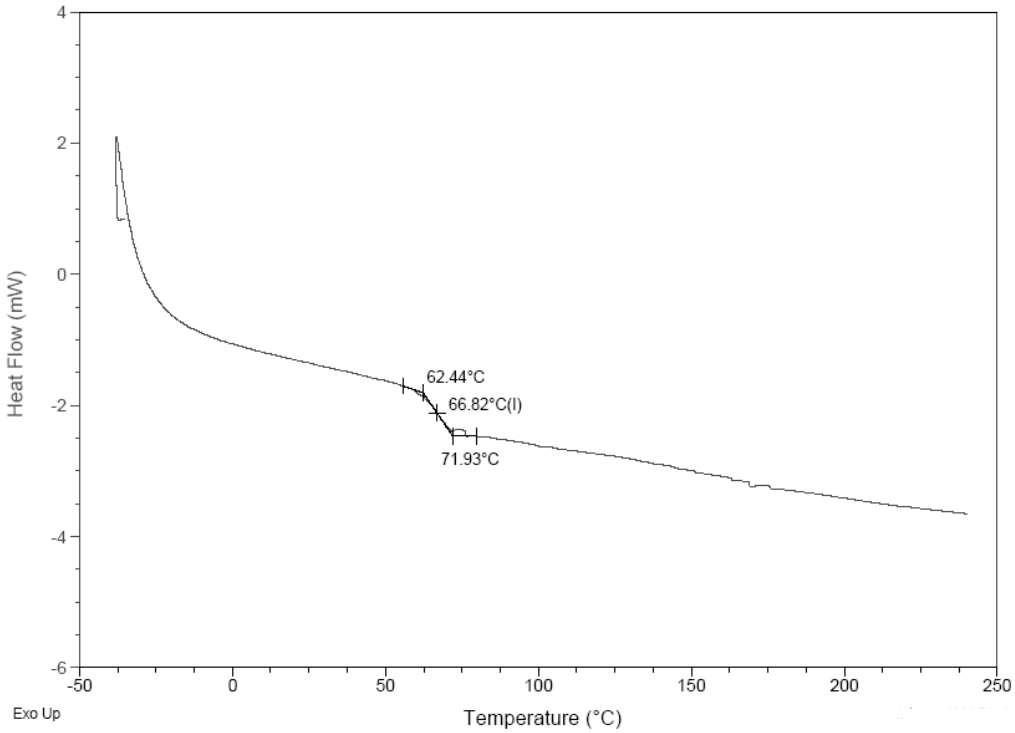

Figure S2-18. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**)-Et_2AlCl catalyst system (NBE 29.7 mol%, ethylene 8 atm, NBE conc. 4.0 M, run 72, Table 5).

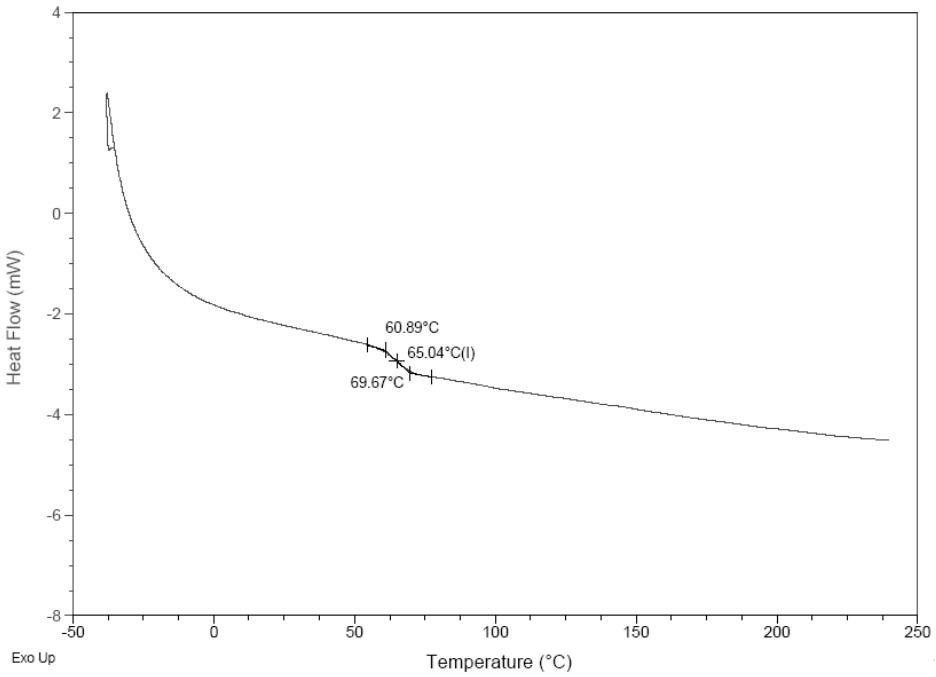

Figure S2-19. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**)-Et_2AlCl catalyst system (NBE 32.5 mol%, ethylene 8 atm, NBE conc. 5.0 M, run 73, Table 5).

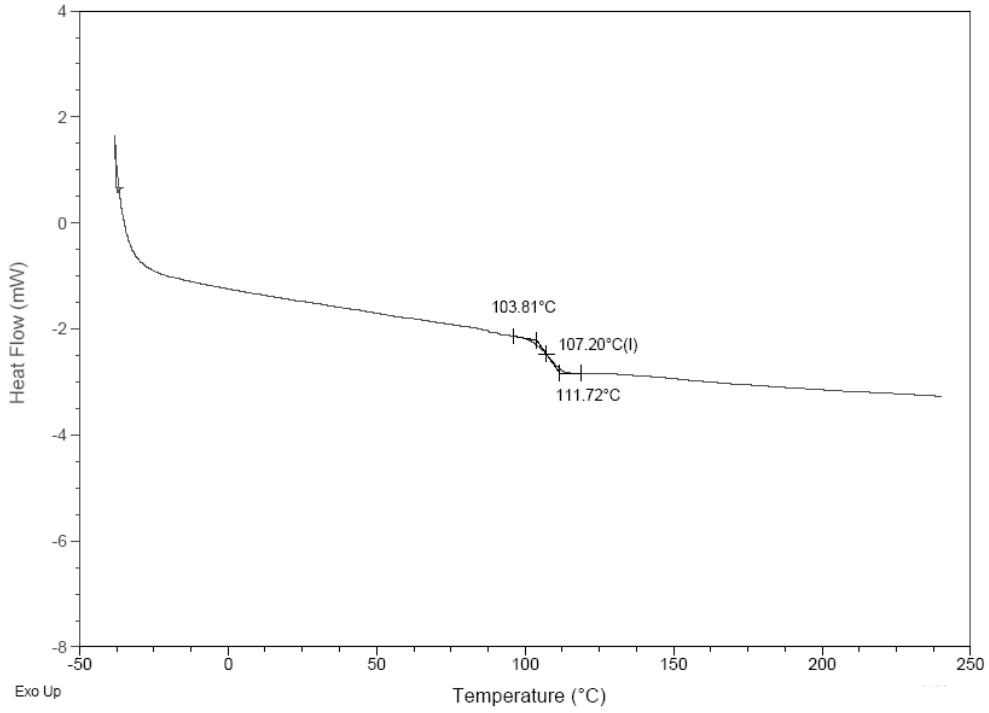

Figure S2-20. DSC thermogram of poly(ethylene-*co*-norbornene) prepared by VCl_2(N-2,6-$Cl_2C_6H_3$)(O-2,6-$Me_2C_6H_3$) (**1a**)-Et_2AlCl catalyst system (NBE 38.8 mol%, ethylene 2 atm, NBE conc. 5.0 M, run 74, Table 5).