Supporting Information

Cycloterpolymerization of 1,6-Heptadiene with Ethylene and Styrene Catalyzed by a THF-Free Half-Sandwich Scandium Complex

Fang Guo, Masayoshi Nishiura, Hiroyuki Koshino, and Zhaomin Hou*

The State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China, and Organometallic Chemistry Laboratory and Advanced Catalyst Research Team, RIKEN Advanced Science Institute, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

E-mail: houz@riken.jp

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SScheme 1. A possible mechanism for the formation of ECP in HPD cyclopolymerization catalyzed by the scandium complexes.

SFigure 1. ^{1}H NMR spectrum (300 MHz, $C_2D_2Cl_4$, r.t.) of a HPD homopolymer prepared by ($C_5Me_4SiMe_3$)Sc(CH_2SiMe_3)$_2$(thf) (**1**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 1).

SFigure 2. ^{13}C NMR spectrum (75.5 MHz, $C_2D_2Cl_4$, r.t.) of a HPD homopolymer prepared by ($C_5Me_4SiMe_3$)Sc(CH_2SiMe_3)$_2$(thf) (**1**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 1).

SFigure 3. ^{1}H NMR spectrum (300 MHz, $C_2D_2Cl_4$, r.t.) of a HPD homopolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 2).

SFigure 4. ^{13}C NMR spectrum (75.5 MHz, $C_2D_2Cl_4$, 100°C) of a HPD homopolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 2).

SFigure 5. ^{1}H NMR spectrum (600 MHz, $C_2D_2Cl_4$, 100°C) of a HPD-ethylene copolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 5).

SFigure 6. ^{13}C NMR spectrum (150 MHz, $C_2D_2Cl_4$, 100°C) of a HPD-ethylene copolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 5).

SFigure 7. DEPT135-^{13}C NMR spectrum (150 MHz, $C_2D_2Cl_4$, 100°C) of a HPD-ethylene copolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 5).

SFigure 8. H2BC NMR spectrum of a HPD-ethylene copolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 5).

SFigure 9. HSQC NMR spectrum of a HPD-ethylene copolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 5).

SFigure 10. HMBC NMR spectrum of a HPD-ethylene copolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 5).

SFigure 11. ^{1}H NMR spectrum (600 MHz, $C_2D_2Cl_4$, 100°C) of a HPD-ethylene-styrene terpolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 10).

SFigure 12. ^{13}C NMR spectra (150 MHz, $C_2D_2Cl_4$, 100°C) of a HPD-ethylene-styrene terpolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 10).

SFigure 13. DEPT 135-^{13}C NMR spectrum (150 MHz, $C_2D_2Cl_4$, 100°C) of a HPD-ethylene-styrene terpolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 10).

SFigure 14. Aliphatic part of ^{13}C NMR spectrum (150 MHz, $C_2D_2Cl_4$, 100°C) of a HPD-ethylene-styrene terpolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 10).

SFigure 15. Aliphatic part of DEPT 135-^{13}C NMR spectrum (150 MHz, $C_2D_2Cl_4$, 100°C) of a HPD-ethylene-styrene terpolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 10).

SFigure 16. Aliphatic part of H2BC NMR spectrum of a HPD-ethylene-styrene terpolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 10).

SFigure 17. Aliphatic part of HSQC NMR spectrum of a HPD-ethylene-styrene terpolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 10).

SFigure 18. Aliphatic part of HMBC NMR spectrum of a HPD-ethylene-styrene terpolymer prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, run 10).

SFigure 19. ^{1}H NMR spectra (300 MHz, $C_2D_2Cl_4$, 100°C) of HPD-ethylene-styrene terpolymers prepared by ($C_5Me_4SiMe_3$)Sc($CH_2C_6H_4NMe_2$-*o*)$_2$ (**2**)/[Ph_3C][B(C_6F_5)$_4$] (Table 1, runs 7-10).

SFigure 20. ^{13}C NMR spectra (75.5 MHz, $C_2D_2Cl_4$, 100°C) of HPD-ethylene-styrene terpolymers prepared by

$(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, runs 7-10).

SFigure 21. GPC curve of a HPD homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(thf)$ (**1**)/ $[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 1).

SFigure 22. GPC curve of a HPD homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/ $[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 2).

SFigure 23. HT-GPC curve of a HPD-ethylene copolymer prepared by prepared by $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(thf)$ (**1**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 3).

SFigure 24. GPC curve of a HPD-ethylene copolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 5).

SFigure 25. HT-GPC curves of HPD-ethylene-styrene terpolymers prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, runs 9 and 11).

SFigure 26. DSC curve of a HPD homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(thf)$ (**1**)/ $[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 1).

SFigure 27. DSC curve of a HPD homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/ $[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 2).

SFigure 28. DSC curve of a HPD-ethylene copolymer prepared by prepared by $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(thf)$ (**1**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 3).

SFigure 29. DSC curve of a HPD-ethylene copolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 5).

SFigure 30. DSC curve of a HPD-ethylene-styrene terpolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 8).

Experimental Section:

General Procedures and Materials. All manipulations of air and moisture-sensitive compounds were performed under a nitrogen atmosphere by use of standard Schlenk techniques or in an Mbraun glovebox. Nitrogen (Takachiho Chemical Industrial Co., Ltd.) was purified by being passed through a Dryclean column (4 A molecular sieves, Nikka Seiko Co.) and a Gasclean CC-XR column (Nikka Seiko Co.). Anhydrous chlorobenzene was purified by use of a SPS-800 solvent purification system (Mbraun), and dried over fresh 4 A molecular sieves in the glovebox. Styrene was purchased from Kanto Chemical Co., Ltd., dried by stirring with CaH_2 for 24 hours, vacuum-transferred, and degassed by two freeze-pump-thaw cycles. 1,6-Heptadiene was purchased from TCI, dried over sodium and tripropyl aluminum, vacuum-transferred, and degassed by two freeze-pump-thaw cycles. $[Ph_3C][B(C_6F_5)_4]$ was purchased from Tosoh Finechem Corporation and used without purification. The deuterated solvents were obtained from ISOTEC. $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(thf)$ (ref. Li, X.; Nishiura, M.; Hu, L.; Mori, K.; Hou, Z. *J. Am. Chem. Soc.* **2009**, *131*, 13870–13882.) and $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (ref. Li, X.; Nishiura, M.; Mori, K.; Mashiko T.; Hou, Z. *Chem. Commun.* **2007**, 4137–4139.) were prepared according to literature methods. 1,1,2,2,-Tetrachloroethane-d_2 (99.6 atom% D) was obtained from Cambridge Isotope. The NMR data of homopolymers, copolymers and terpolymers were obtained on JEOL JNM-EX 300 and JNM-ECA 600 spectrometer in 1,1,2,2,-tetrachloroethane-d_2 at room temperature or 100 °C. The molecular weights and the molecular weight distributions of HPD homopolymers and HPD-ethylene copolymers were determined at 40 °C by gel permeation chromatography (GPC) on a HLC-8220 GPC apparatus (Tosoh Corporation). THF was employed as an eluent at a flow rate of 0.35 mL/min. The calibration was made by polystyrene standard. The molecular weights and the molecular weight distributions of HPD-ethylene-styrene terpolymers were determined at 145 °C by high temperature gel permeation chromatography (HT-GPC) on a HLC-8121GPC/HT apparatus (Tosoh Corporation). 1,2-Dichlorobenzene (DCB) was employed as an eluent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard. The DSC measurements were performed on a DSC6220 (SII Co.) at a rate of 20 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to 300 °C, cooling at 20 °C/min to -50 °C, and then recording the second DSC scan.

A Typical Procedure for 1,6-Heptadiene (HPD) Polymerization (Table 1, run 2). In a glovebox, 1,6-heptadiene (914 mg, 9.5 mmol) was added under vigorous stirring to a reaction mixture of $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (10 mg, 19 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (18 mg, 19 μmol) in chlorobenzene (6 mL). The polymerization was terminated by addition of methanol after 20 min. The resulting mixture was poured into a large amount of methanol to precipitate the polymer product, which was then collected by filtration, washed with methanol and dried under vacuum at 60 °C to a constant weight. The ratio of MCH and ECP units in the HPD homopolymer was calculated according to the formula: *cis*-MCH/*trans*-MCH/*cis*-ECP/*trans*-ECP = $I_1/I_2/I_3/I_4$, in which I_1 is the integration of the resonance at 26.42 ppm (one methylene carbon of the *cis*-MCH unit), I_2 is the integration of the resonance at 21.16 ppm (one methylene carbon of the *trans*-MCH unit), I_3 is the integration of the resonance at 22.56 ppm (one methylene carbon of the *cis*-ECP unit), and I_4 is the integration of the resonance at 23.85 ppm (one methylene carbon of the *trans*-ECP unit) in the ^{13}C NMR spectrum.

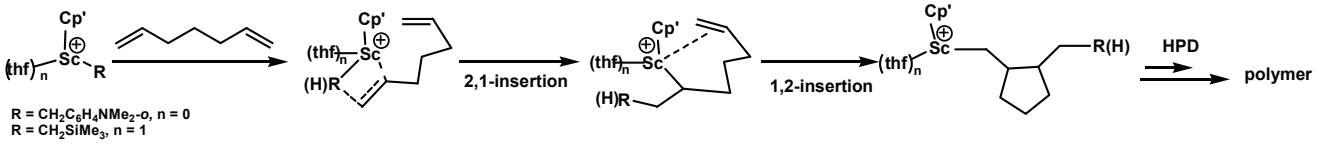
A Typical Procedure for the Copolymerization of 1,6-Heptadiene (HPD) with Ethylene (Et) (Table 1, run 4). In a glovebox, a chlorobenzene solution (1 mL) of 1,6-heptadiene (548 mg, 5.7 mmol) was charged into a two-necked flask with a magnetic stir-bar. The flask was taken outside and connected to a well-purged Schlenk ethylene line and a mercury-sealed stopper by use of a three-way cock. Ethylene (1 atm) was introduced into the system and was saturated in the solution by stirring for 2 min. A chlorobenzene solution (1 mL) of $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (10 mg, 19 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (18 mg, 19 μmol) was then added through a syringe under vigorous stirring. The polymerization was quenched after 3 min by addition of methanol. The polymer product was collected by filtration, washed with methanol, and dried under vacuum at 60 °C to a constant weight. The Et, MCH and ECP contents of the HPD-ethylene copolymer were

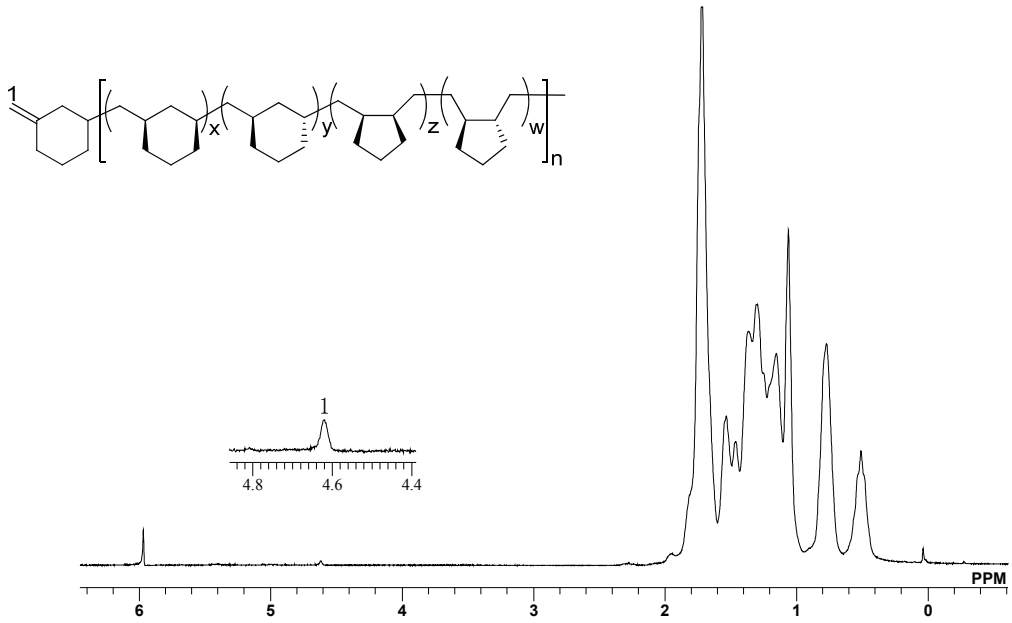
calculated according to the formula: Et mol% = $\{(0.5I_5+I_6+I_7+I_8)/(0.5I_5+I_6+I_7+I_8+I_1+I_2+I_3+I_4)\}\times100$, *cis*-MCH/*trans*-MCH/*cis*-ECP/*trans*-ECP = $I_1/I_2/I_3/I_4$, where I_1, I_2, I_3 and I_4 are defined as above, I_5 is the integration of the resonance at 29.47 ppm (the two methylene carbons of Et blocks), I_6 is the integration of the resonance at 29.88 ppm (one methylene carbon of an Et unit connected to MCH), I_7 is the integration of the resonance at 23.94 ppm (one methylene carbon of an Et unit between two MCH units), I_8 is the integration of the resonance at 24.47 ppm (one methylene carbon of an Et unit between two MCH units) in the ^{13}C NMR spectrum.

An Attempt to Copolymerize 1,6-Heptadiene (HPD) with Styrene (Table 1, run 6). In a glovebox, a mixture of 1,6-heptadiene (548 mg, 5.7 mmol) and styrene (396 mg, 3.8 mmol) was added under vigorous stirring to a reaction mixture of $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (10 mg, 19 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (18 mg, 19 μmol) in chlorobenzene (6 mL). The polymerization was terminated by addition of methanol after 20 min. The resulting mixture was poured into a large amount of methanol to precipitate the polymer product, which was then collected by filtration, washed with methanol and dried under vacuum at 60 °C to a constant weight. Solvent extraction experiments revealed that the product is a mixture of homopoly(HPD) and syndiotactic homopolystyrene.

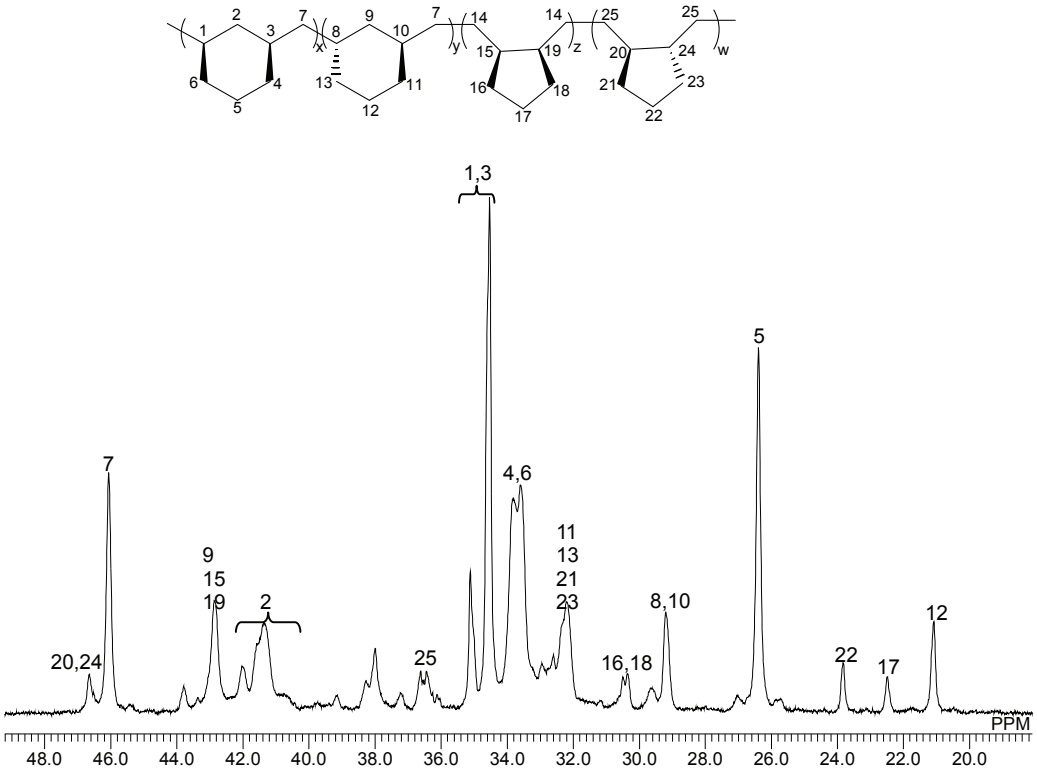
A Typical Procedure for the Terpolymerization of 1,6-Heptadiene (HPD) with Ethylene and Styrene (Table 1, run 9). In a glovebox, a toluene solution (1 mL) of 1,6-heptadiene (548 mg, 5.7 mmol) and styrene (396 mg, 3.8 mmol) was charged into a two-necked flask with a magnetic stir-bar. The flask was taken outside and connected to a well-purged Schlenk ethylene line and a mercury-sealed stopper by use of a three-way cock. Ethylene (1 atm) was introduced into the system and was saturated in the solution by stirring for 2 min. A toluene solution (1 mL) of $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (10 mg, 19 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (18 mg, 19 μmol) was then added by a syringe under vigorous stirring. The polymerization was quenched after 2 min by addition of methanol. The polymer product was collected by filtration, washed with methanol, and dried under vacuum at 60 °C to a constant weight. The St, Et, MCH and ECP contents of the HPD-ethylene-styrene terpolymer were calculated according to the formula: Et/HPD (molar ratio) = $(0.5I_5+I_6+I_7+I_8+I_9)/(I_1+I_2+I_3+I_4) = I$, St mol% = $\{0.2I_{10}/[0.2I_{10}+(I+1)(I_{11}-0.6I_{10})/(4I+12)]\}\times100$, Et mol% = $\{[I(I_{11}-0.6I_{10})/(4I+12)]/[0.2I_{10}+(I+1)(I_{11}-0.6I_{10})/(4I+12)]\}\times100$, HPD mol% = 100−St mol%−Et mol%, MCH/ECP (molar ratio) = $(I_1+I_2)/(I_3+I_4)$, where I_1–I_8 are defined as above, I_9 is the integration of the resonance at 37.07 ppm (one methylene carbon of an Et unit connected to St), I_{10} is the integration of the resonances at 6.5–7.5 ppm (five phenyl protons of the St unit) in the ^1H NMR spectrum, I_{11} is the integration of the resonance from 0.5–2.2 ppm (twelve protons from HPD monomer, three protons of the St unit and four protons of the Et unit) in the ^1H NMR spectrum.

SScheme 1. A possible mechanism for the formation of the five-member ring ECP units in the cyclopolymerization of HPD catalyzed by scandium complexes

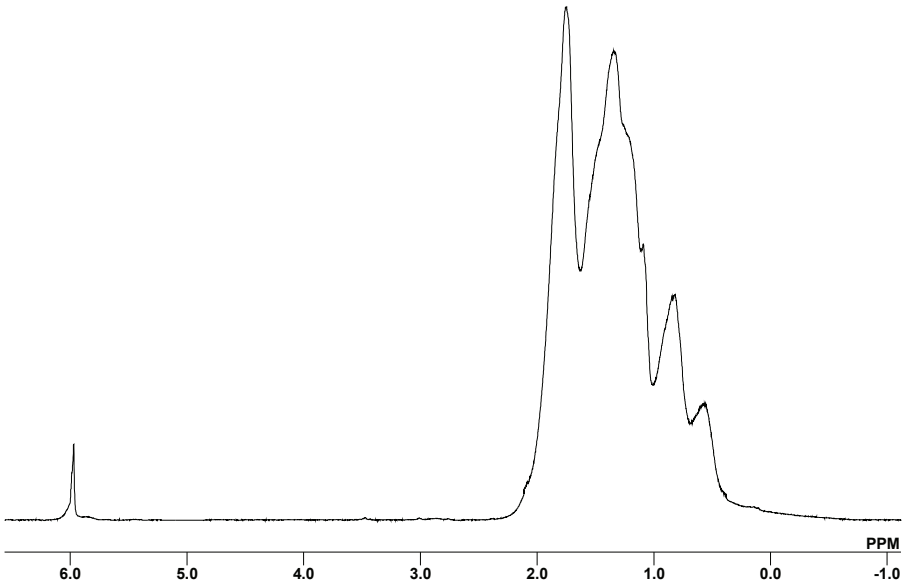




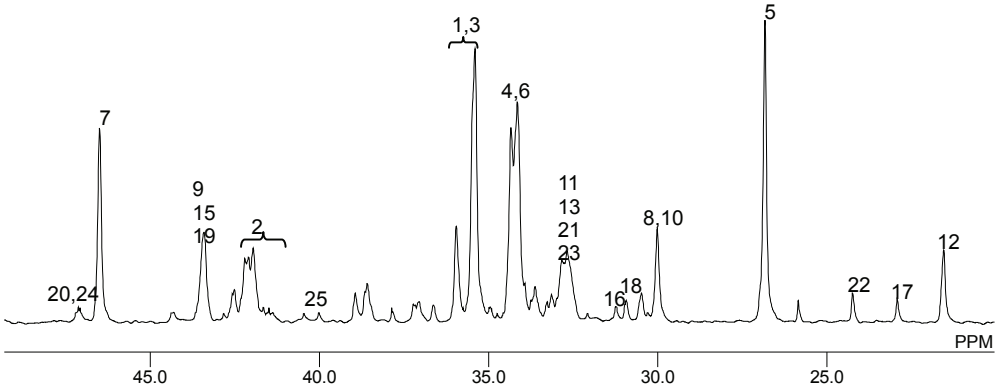
SFigure 1. ^{1}H NMR spectrum (300 MHz, $C_2D_2Cl_4$, r.t.) of a HPD homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(thf)$ (**1**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 1).



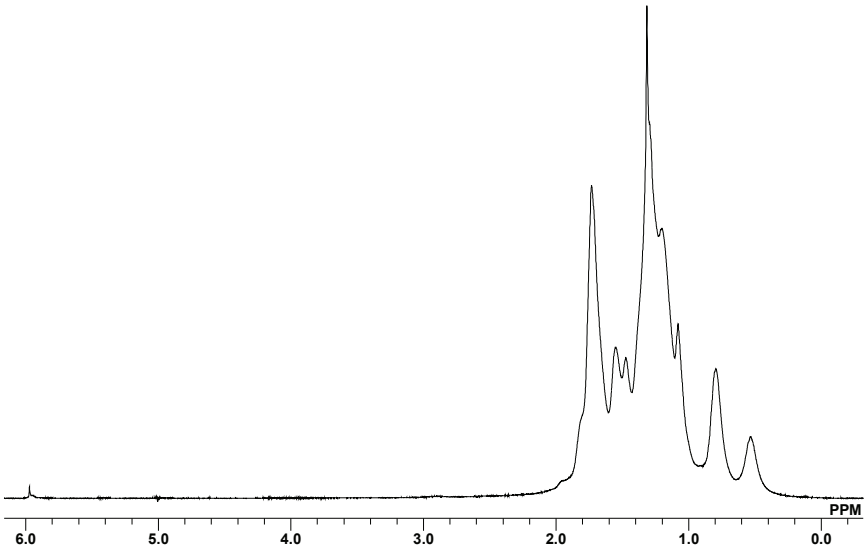
SFigure 2. ^{13}C NMR spectrum (75.5 MHz, $C_2D_2Cl_4$, r.t.) of a HPD homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(thf)$ (**1**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 1).



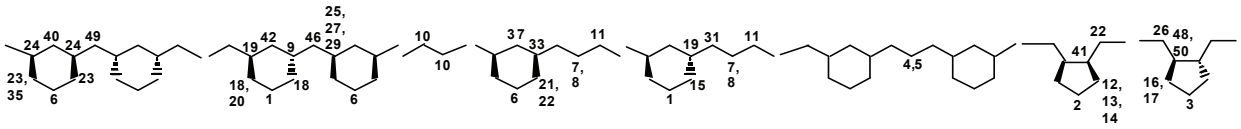
SFigure 3. ^{1}H NMR spectrum (300 MHz, $C_2D_2Cl_4$, r.t.) of a HPD homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 2).

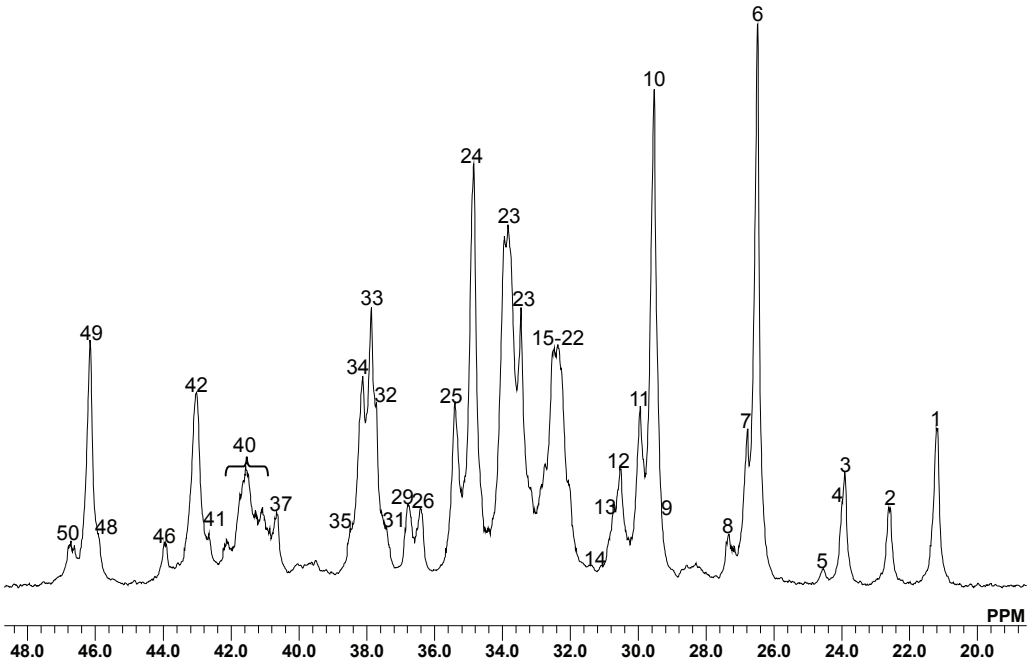


SFigure 4. ^{13}C NMR spectrum (75.5 MHz, $C_2D_2Cl_4$, 80 °C) of a HPD homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 2).

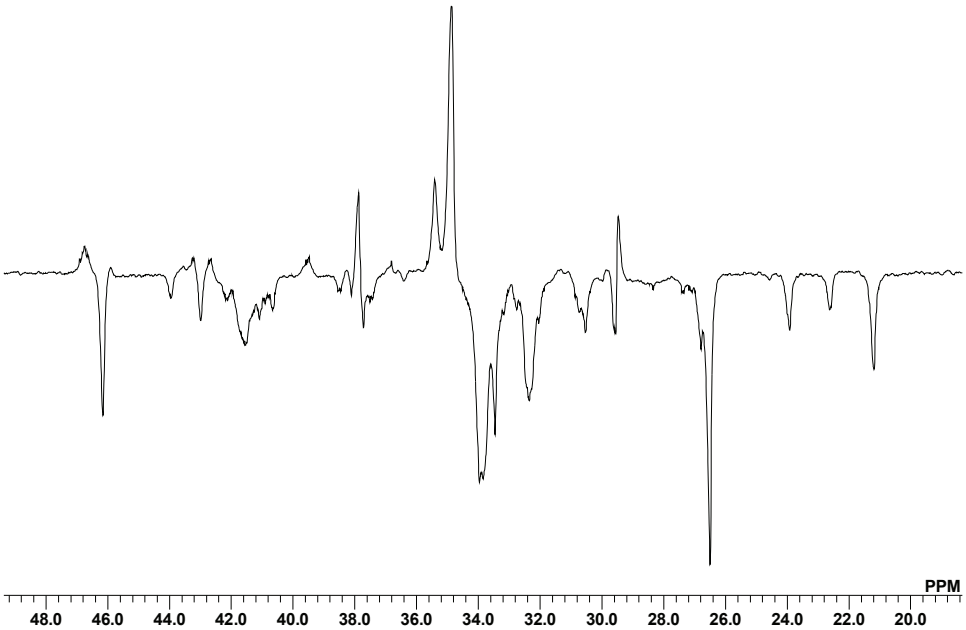


SFigure 5. ^{1}H NMR spectrum (600 MHz, $C_2D_2Cl_4$, 100 °C) of a HPD-ethylene copolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 5).

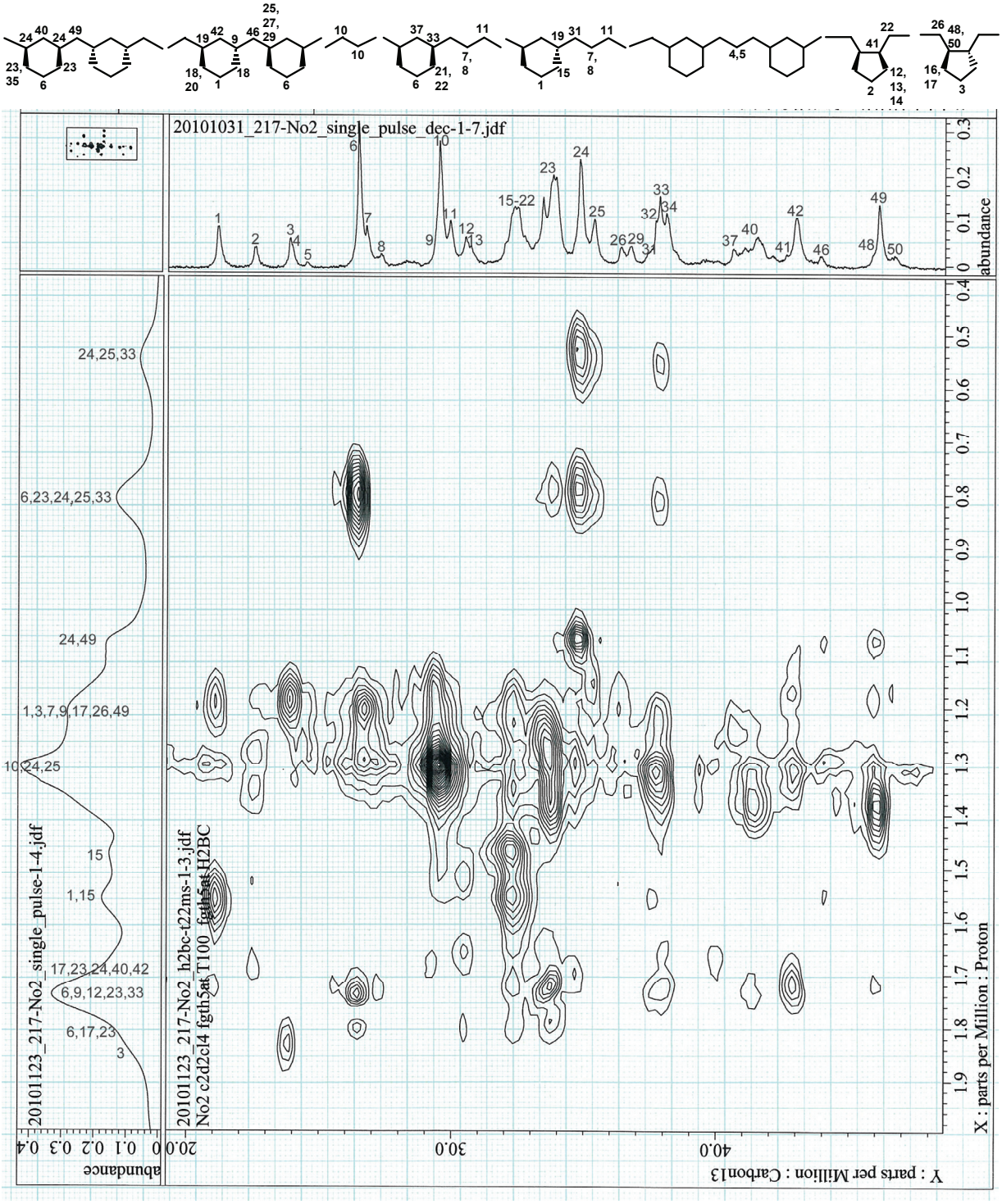




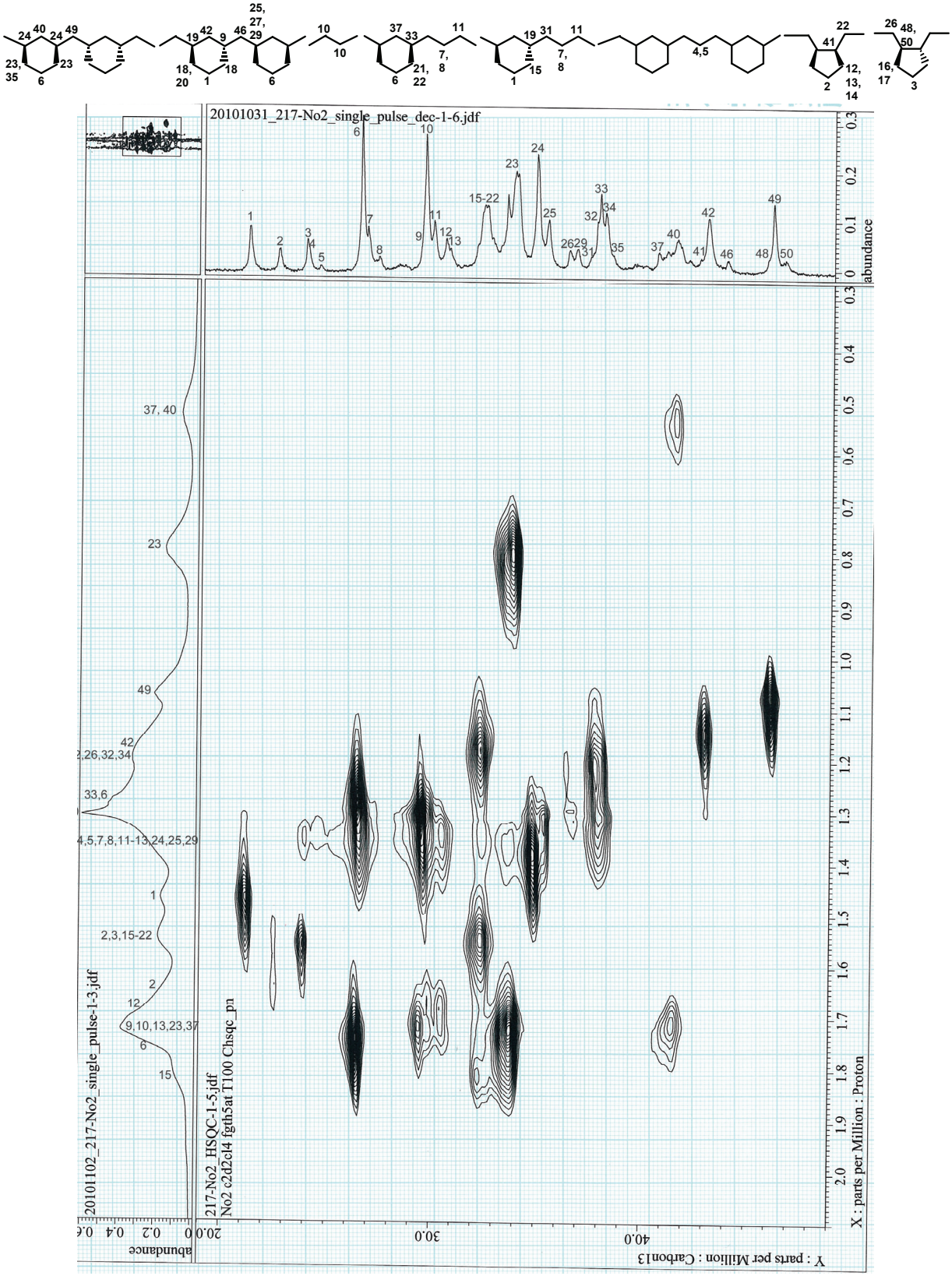
SFigure 6. ^{13}C NMR spectrum (150 MHz, $C_2D_2Cl_4$, 100 °C) of a HPD-ethylene copolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 5).



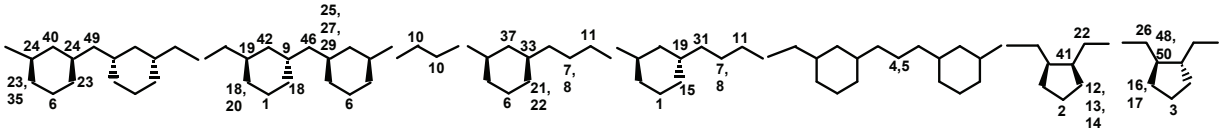
SFigure 7. DEPT135-^{13}C NMR spectrum (150 MHz, $C_2D_2Cl_4$, 100 °C) of a HPD-ethylene copolymer preparedby $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 5).

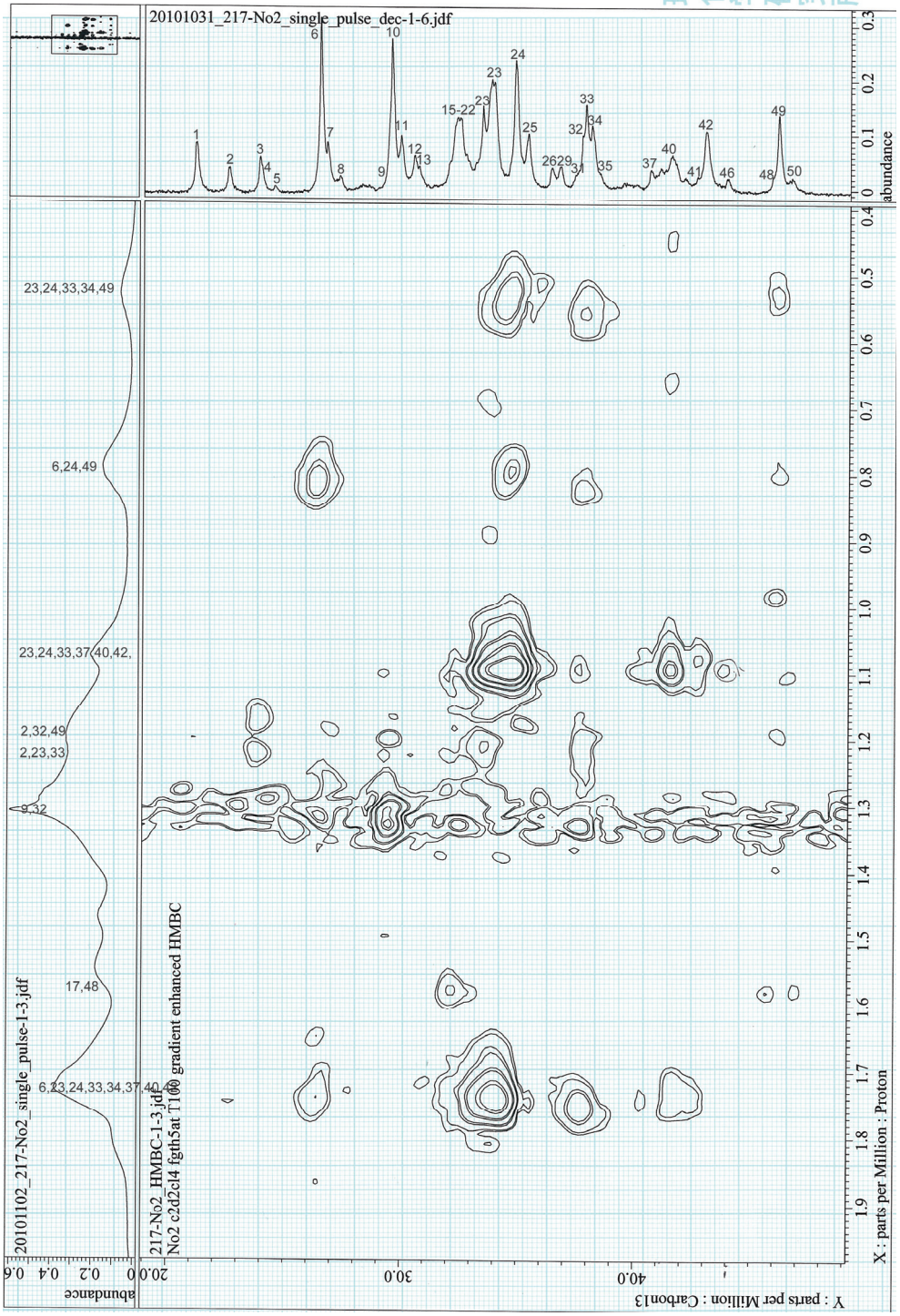


SFigure 8. H2BC NMR spectrum of a HPD-ethylene copolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 5).

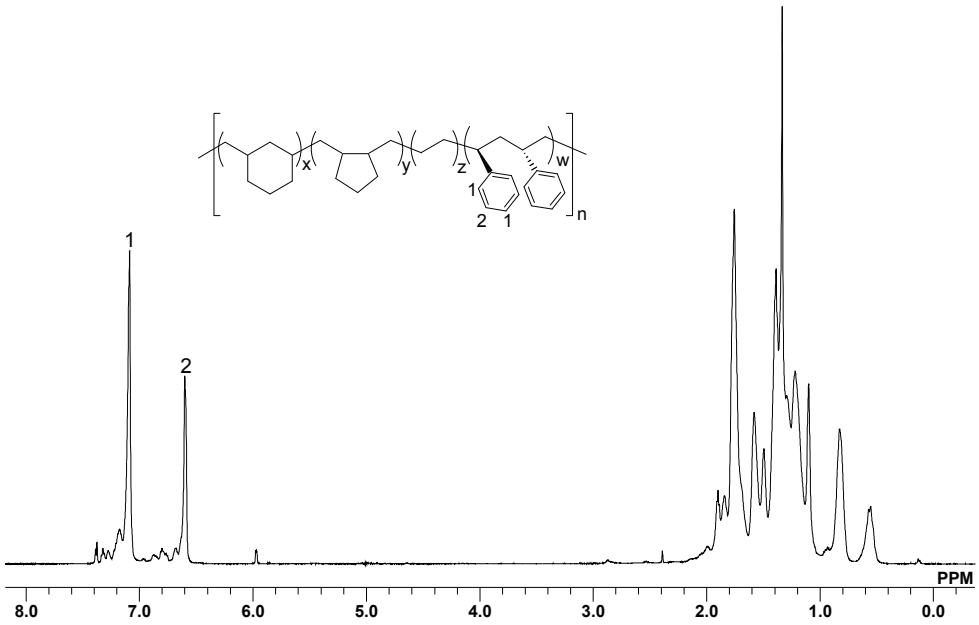


SFigure 9. HSQC NMR spectrum of a HPD-ethylene copolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 5).

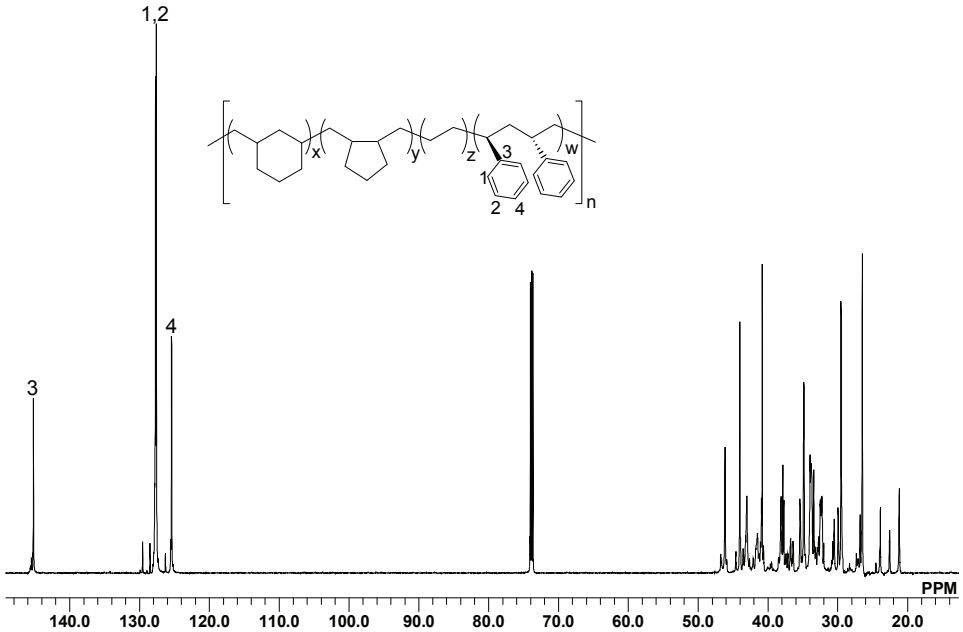




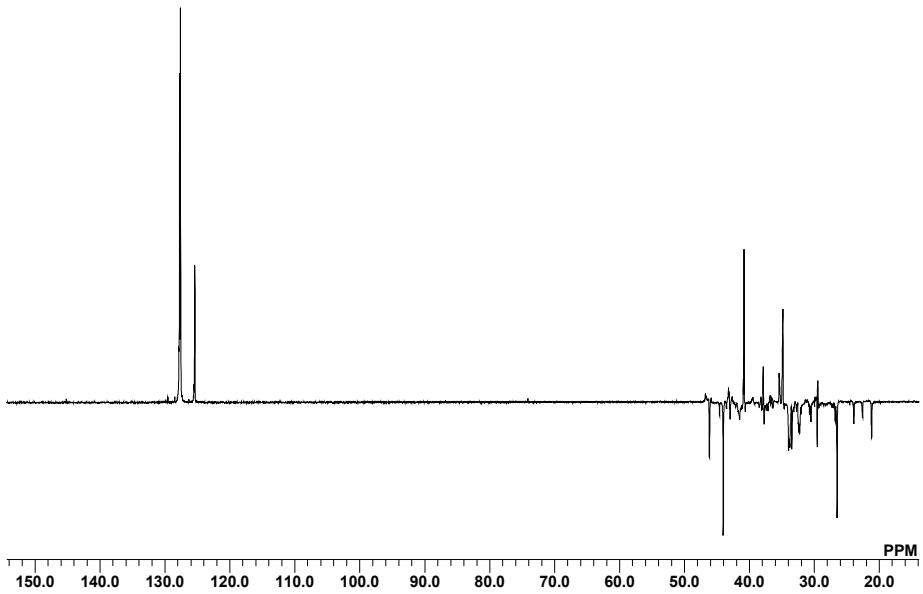
SFigure 10. HMBC NMR spectrum of a HPD-ethylene copolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 5).



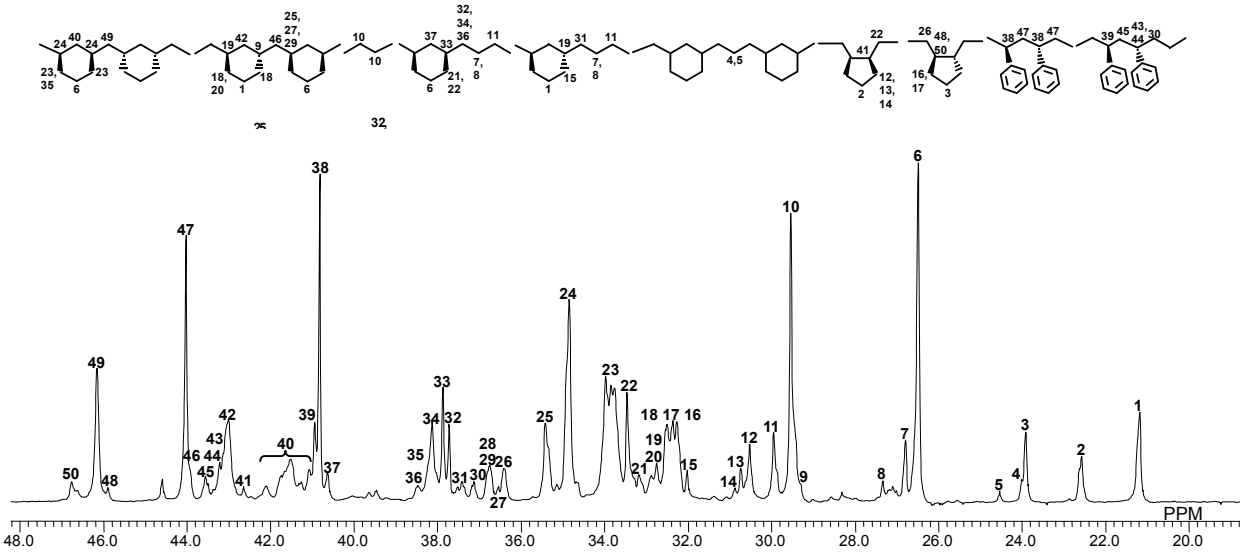
SFigure 11. ^{1}H NMR spectrum (600 MHz, $C_2D_2Cl_4$, 100 °C) of a HPD-ethylene-styrene terpolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run10).



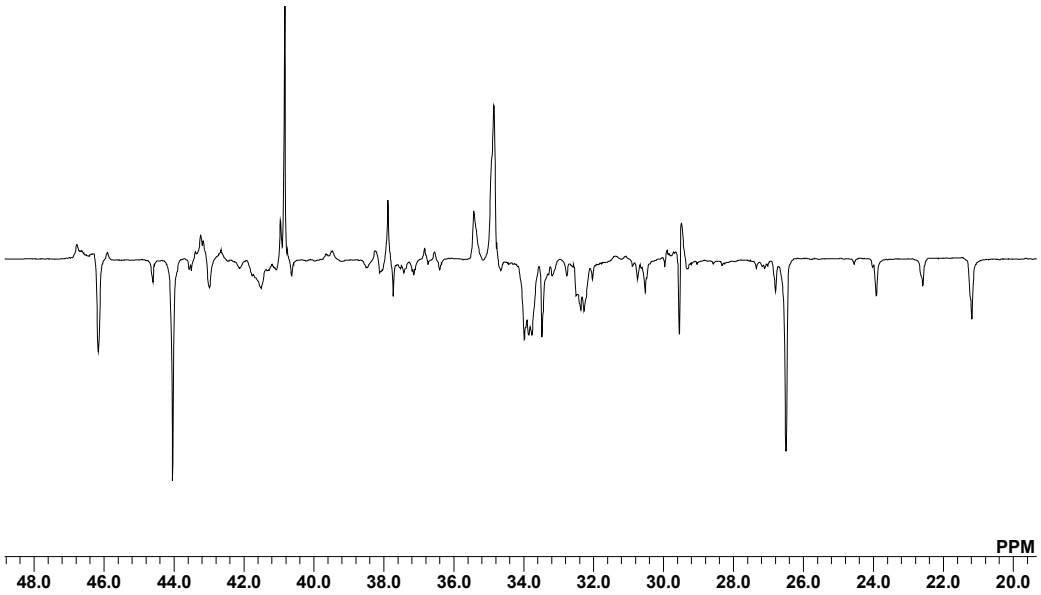
SFigure 12. ^{13}C NMR spectrum (150 MHz, $C_2D_2Cl_4$, 100 °C) of a HPD-ethylene-styrene terpolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run10).



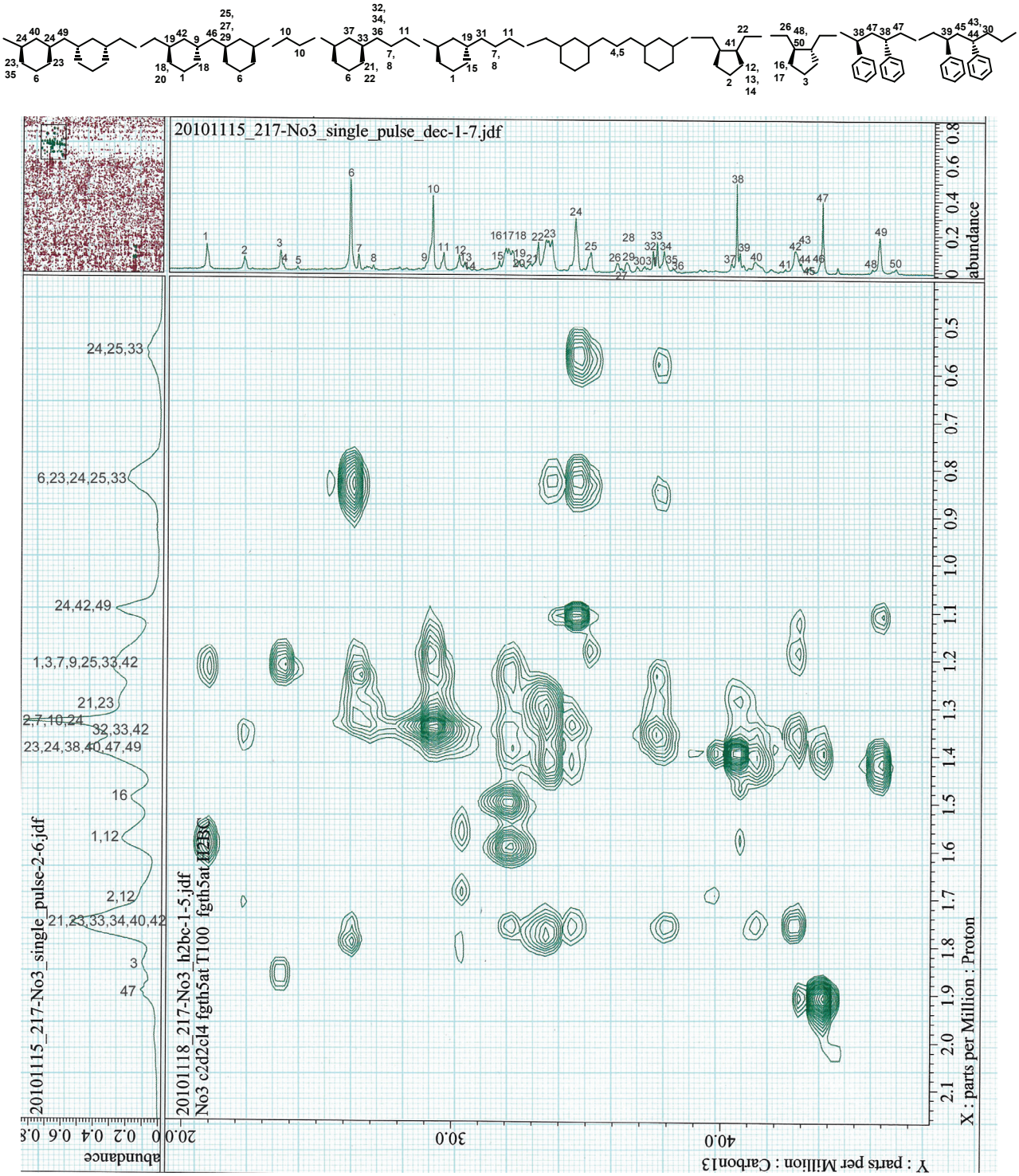
SFigure 13. DEPT 135-^{13}C NMR spectrum (150 MHz, $C_2D_2Cl_4$, 100 °C) of a HPD-ethylene-styrene terpolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run10).



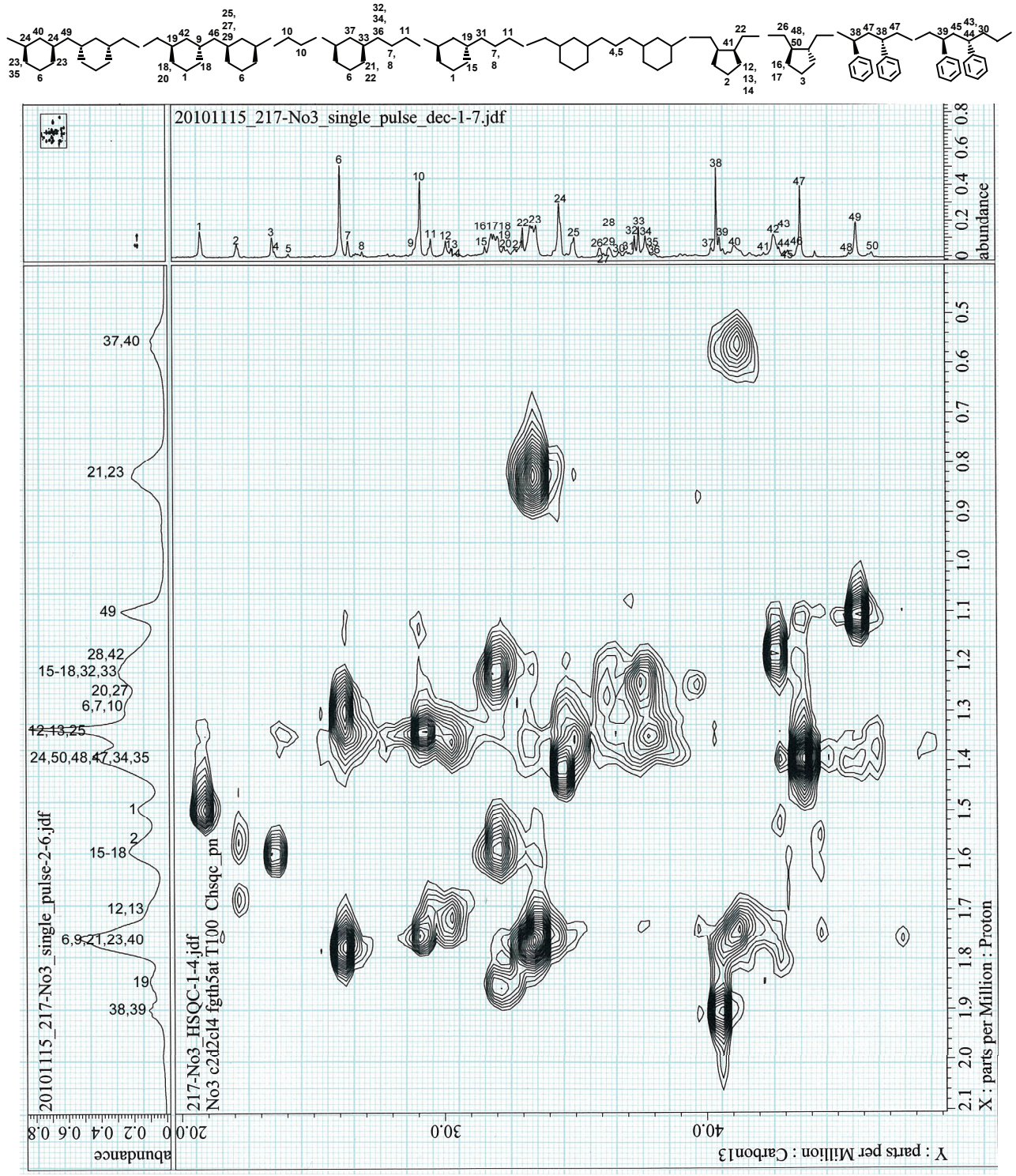
SFigure 14. Aliphatic part of the ^{13}C NMR spectrum (150 MHz, $C_2D_2Cl_4$, 100 °C) of a HPD-ethylene-styrene terpolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run10).



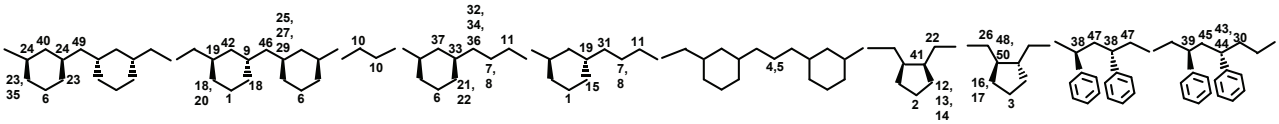
SFigure 15. Aliphatic part of the DEPT 135-^{13}C NMR spectrum (150 MHz, $C_2D_2Cl_4$, 100 °C) of a HPD-ethylene-styrene terpolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/ $[Ph_3C][B(C_6F_5)_4]$ (Table 1, run10).

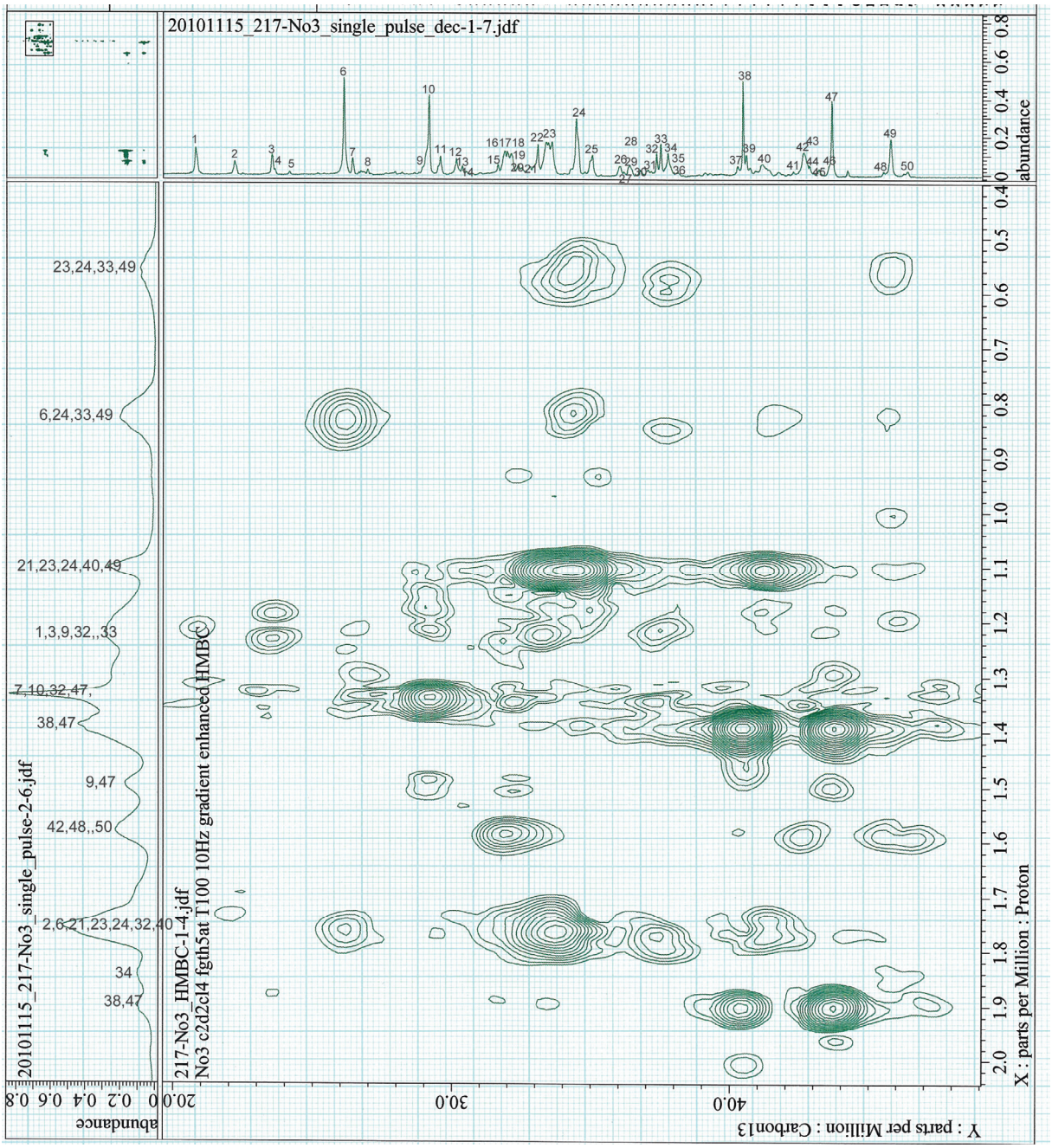


SFigure 16. Aliphatic part of the H2BC NMR spectrum of a HPD-ethylene-styrene terpolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run10).

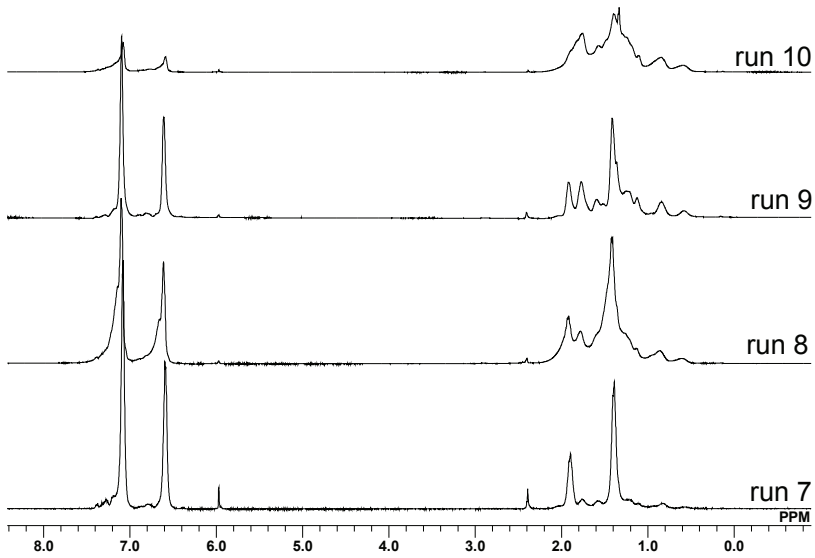


SFigure 17. Aliphatic part of the HSQC NMR spectrum of a HPD-ethylene-styrene terpolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run10).

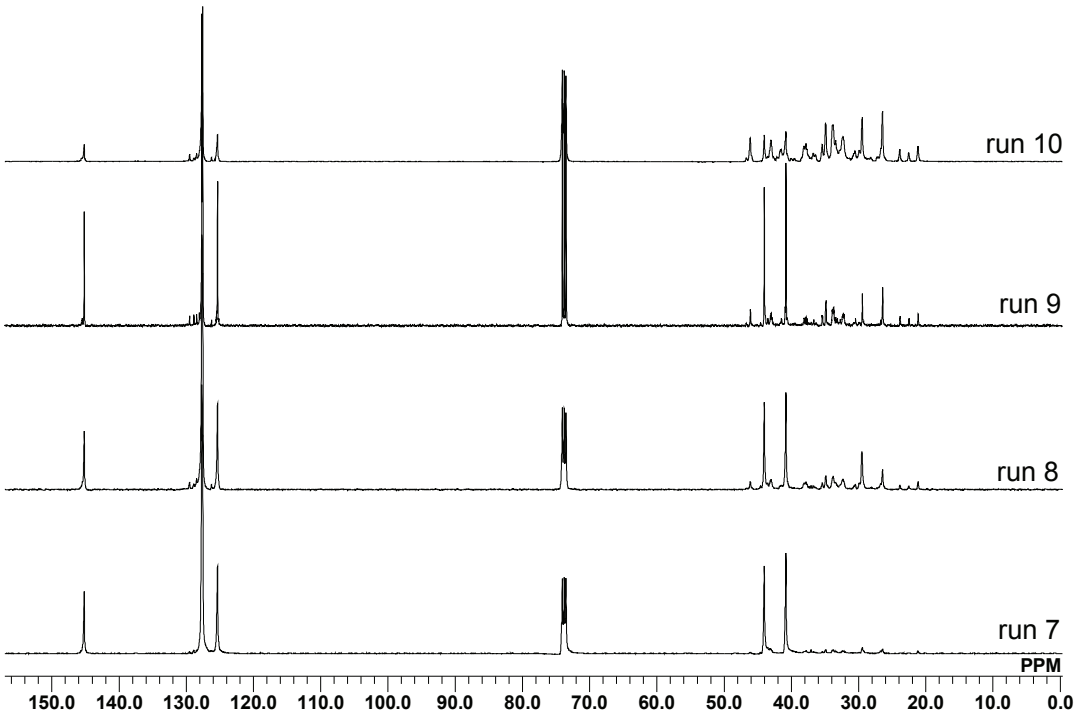




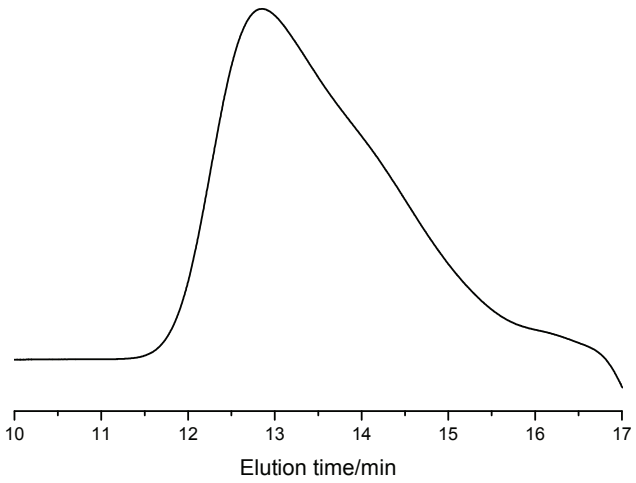
SFigure 18. Aliphatic part of the HMBC NMR spectrum of a HPD-ethylene-styrene terpolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run10).



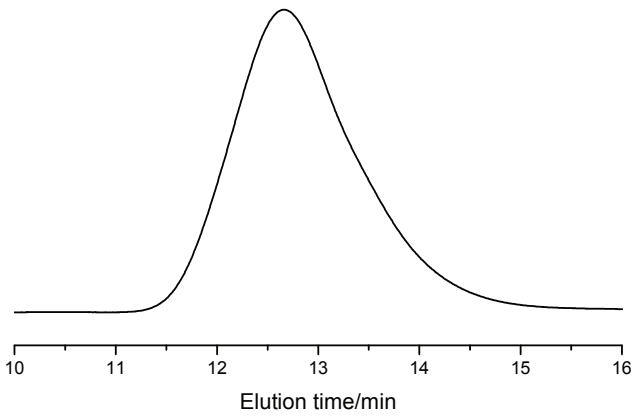
SFigure 19. ^{1}H NMR spectra (300 MHz, $C_2D_2Cl_4$, 100 °C) of HPD-ethylene-styrene terpolymers prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, runs 7-10).



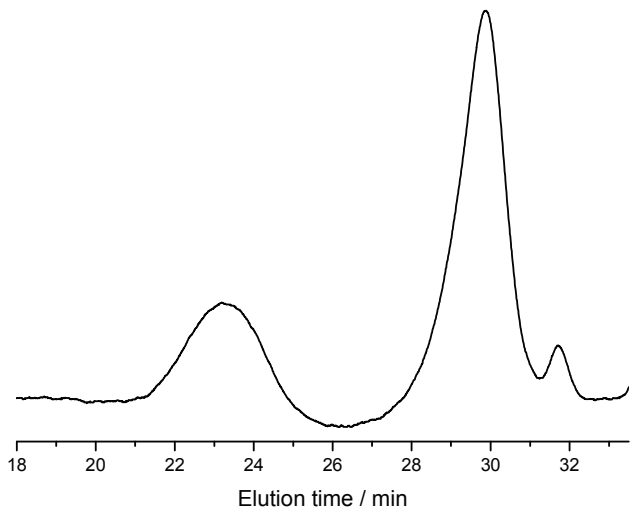
SFigure 20. ^{13}C NMR spectra (75,5 MHz, $C_2D_2Cl_4$, 100°C) of HPD-ethylene-styrene terpolymers prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, runs 7-10).



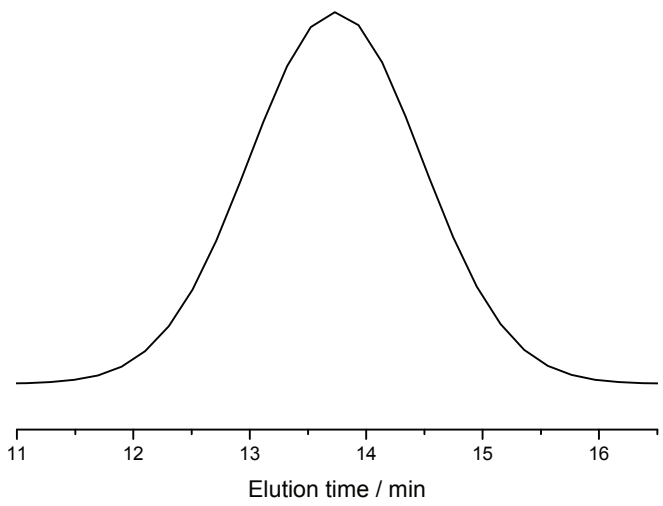
SFigure 21. GPC curve of a HPD homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(thf)$ (**1**)/ $[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 1).



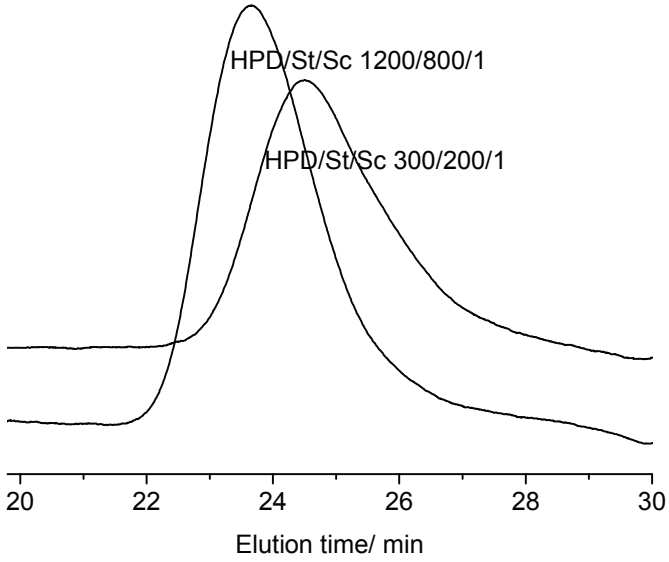
SFigure 22. GPC curve of a HPD homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/ $[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 2).



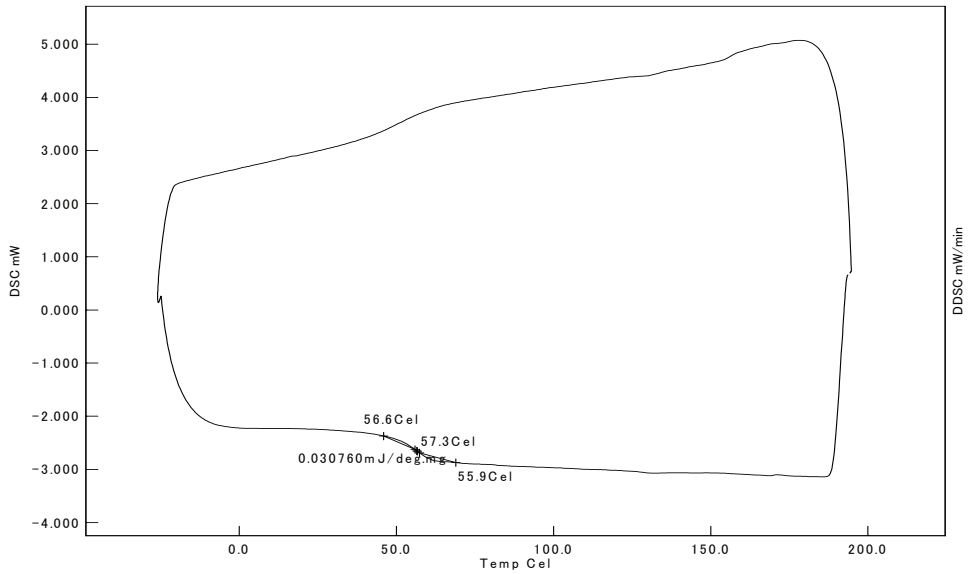
SFigure 23. HT-GPC curve of the *o*-dichlorobenezene-soluble (130 °C) part of the HPD-ethylene copolymer products prepared by ($C_5Me_4SiMe_3$) $Sc(CH_2SiMe_3)_2$(thf) (**1**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 3).



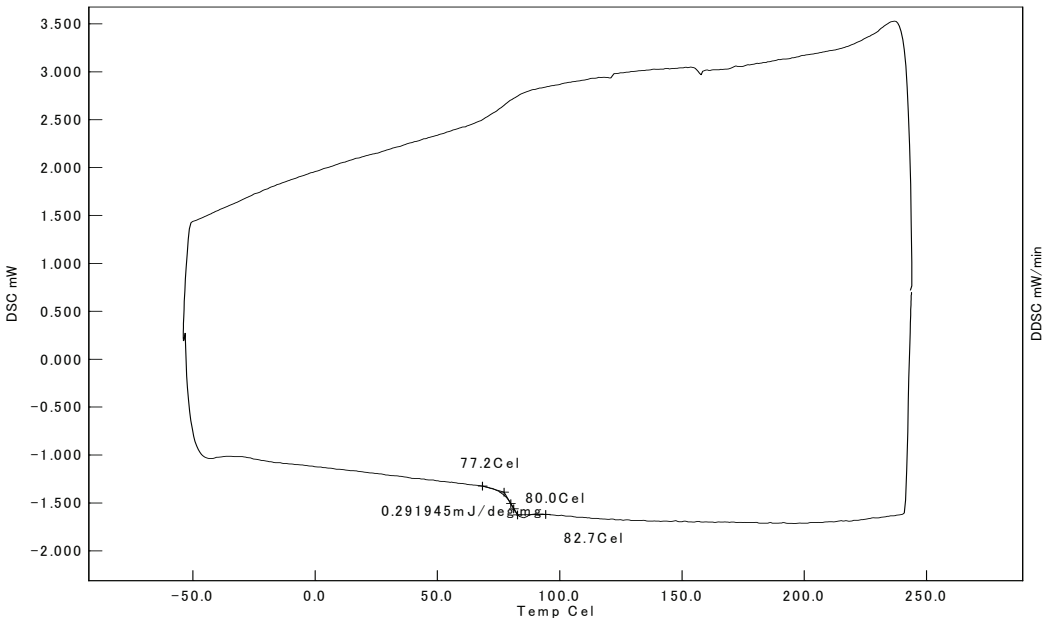
SFigure 24. GPC curve of a HPD-ethylene copolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 5).



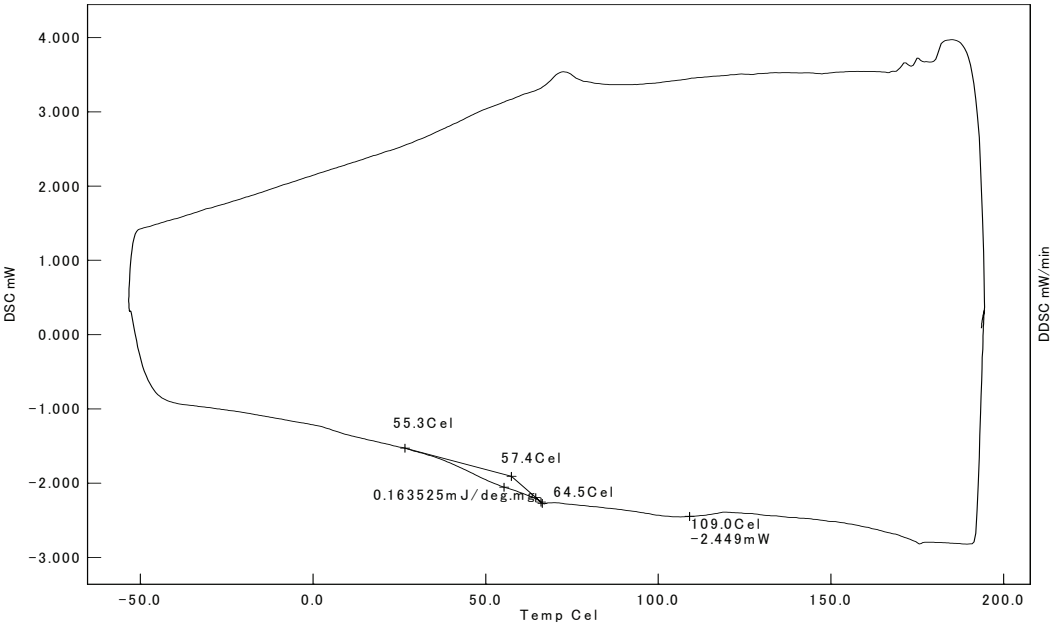
SFigure 25. HT-GPC curves of HPD-ethylene-styrene terpolymers prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, runs 9 and 11).



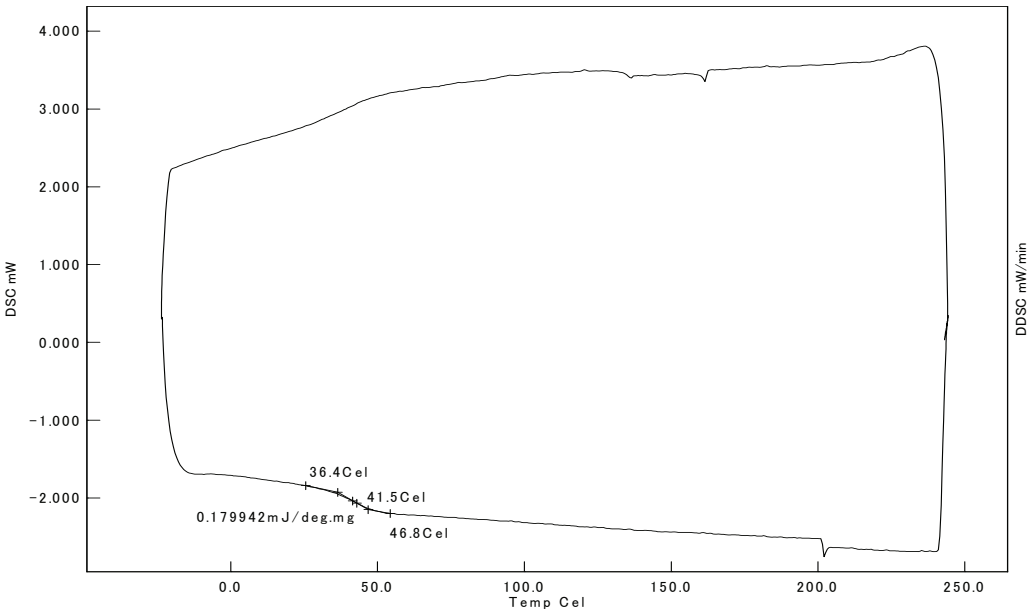
SFigure 26. DSC curve of a HPD homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(thf)$ (**1**)/ $[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 1).



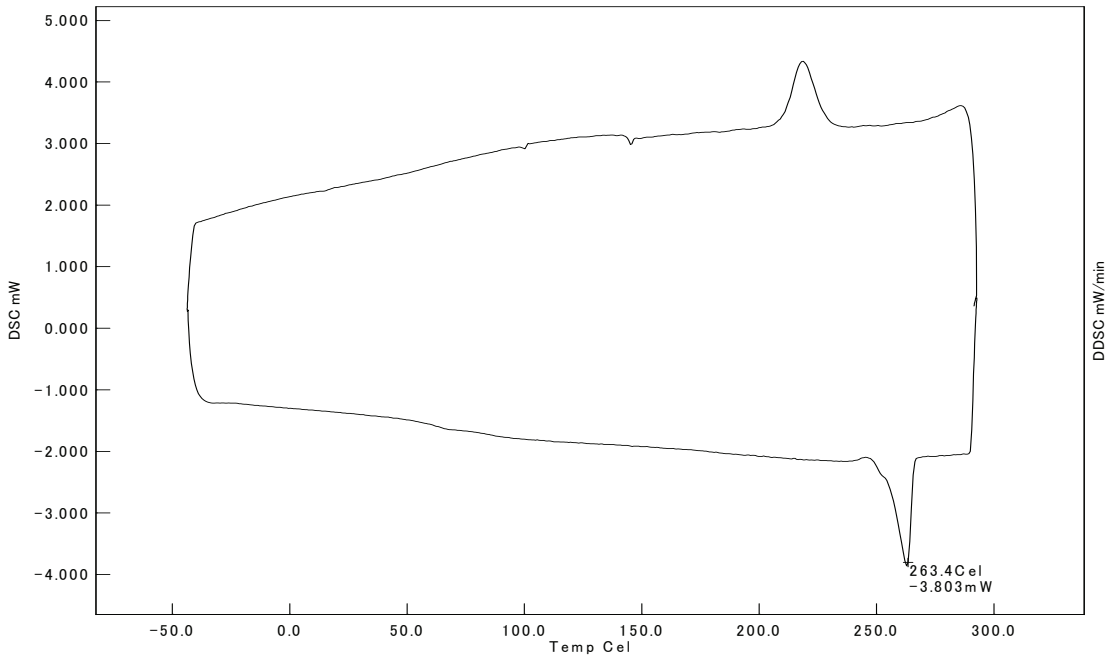
SFigure 27. DSC curve of a HPD homopolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/ $[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 2).



SFigure 28. DSC curve of the *o*-dichlorobenezene-soluble (130 °C) part of the HPD-ethylene copolymer products prepared by $(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(thf)$ (**1**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 3).



SFigure 29. DSC curve of a HPD-ethylene copolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 5).



SFigure 30. DSC curve of a HPD-ethylene-styrene terpolymer prepared by $(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**2**)/$[Ph_3C][B(C_6F_5)_4]$ (Table 1, run 8).