Supporting Information

Regio- and stereospecific living polymerization and copolymerization of (*E*)-1,3-pentadiene with 1,3-butadiene by half-sandwich scandium catalysts

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Experimental section

General procedures and materials. All the manipulations were performed under pure nitrogen with rigorous exclusion of air and moisture using standard Schlenk techniques and an Mbraun glovebox. Nitrogen was purified by being passed through a Dryclean column (4A molecular sieves, Nikka Seiko Co.) and a Gasclean CC-XR column (Nikka Seiko Co.). Solvent were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na Chips in a glovebox. Half-sandwich scandium dialkyl complexes (**1**–**4**) were prepared as described previously (N. Yu, M. Nishiura, X. Li, Z. Xi, Z. Hou, *Chem. Asian J.*, 2008, **3**, 1406. X. Li, M. Nishiura, Li. Hu, K. Mori, Z. Hou, *J. Am. Chem. Soc.*, 2009, **131**, 13870.). $[PhNMe_2H][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$ and $B(C_6F_5)_3$ were purchased from Tosoh Finechem Corporation. (*E*)-1,3-Pentadiene (Aldrich) and 1,3-butadiene (Aldrich) were dried by stirring with MS-4A (Aldrich) for 24 hours. (*Z*)-1,3-Pentadiene (TCI) dried over CaH_2, vacuum-transferred and degassed by two freeze-pump-thaw cycles prior to polymerization experiments. The deuterated solvents were obtained from ISOTEC. ^1H, ^{13}C NMR and ^1H–^{13}C HMQC spectra were recorded on JEOL EX270 (270 MHz for ^1H; 67 MHz for ^{13}C) spectrometer and JEOL ECA400WB (400 MHz for ^1H; 100 MHz for ^{13}C). All deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere. The microstructure of the polypentadiene (PPD) and polybutadiene (PBD) products were determined by ^1H and ^{13}C NMR spectroscopy in $CDCl_3$ (and C_6D_6) solution at 25 °C. Molecular weight and molecular weight distribution for the polymer were measured by gel permeation chromatography (GPC, Tosoh HLC-8220 GPC, Column: Super HZM-H HT × 3) at 40 °C using THF as an eluent at a flow rate of 0.35 mL/min. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples. The DSC measurements were performed on a DSC6220 (SII Co.) at a rate of 20 °C/min.

A typical procedure for polymerization of (*E*)-1,3-pentadiene (Table S1, run 1) In the glove box, a predetermined amount of (*E*)-1,3-pentadiene, and 40 μmol of $[PhNMe_2H][B(C_6F_5)_4]$ (13 mg) in toluene were introduced sequentially at room temperature in a 30 mL round-bottom glass flask with a stirring bar. A few minutes later, 40 μmol of complex **4** (13 mg) in toluene was added into the flask. The polymerization was carried out for a predetermined period of time, and was terminated by addition of 2 mL of methanol. The resulting mixture was poured into methanol (100 mL) to precipitate the polymer product. The polymer was collected by filtration and dried under vacuum at 60 °C to a constant weight. The microstructure of the PPD was determined by ^1H and ^{13}C NMR spectroscopy in $CDCl_3$ (and C_6D_6) solution at 25 °C. ^1H NMR (PPD): δ = 0.85–0.94 ($-CH_3$ of 1,4-PPD unit), 1.10–1.32 ($-CH_2-$ of 1,2-PPD unit), 1.61–1.70 ($-CH_3$ of 1,2-PPD unit), 1.89–2.18 (–CH– of 1,2-PPD unit and $-CH_2-$ of 1,4-PPD unit), 2.42–2.55 (–CH– of 1,4-PPD unit), 5.11–5.35 ppm (–CH= of 1,2-PPD unit and –CH= of 1,4-PPD unit). ^{13}C NMR (PPD): δ = 17.96 (*syndiotactic-trans*-1,2-PPD unit), 20.91 (*isotactic-cis*-1,4-PPD unit), 32.29 (*isotactic-cis*-1,4-PPD unit), 35.15 (*isotactic-cis*-1,4-PPD unit), 40.44 (*isotactic-trans*-1,4-PPD unit), 123.90–127.91 and 135.52–137.35 ppm (1,2-PPD unit and 1,4-PPD unit).

The isomer contents of the polypentadiene products were calculated from the ^1H and ^{13}C NMR spectra according to the following formulas (eqs 1–4):

$$\text{Mol 1,4-PD\%} = \{I_{H5}/(I_{H5} + I_{H5v})\} \times 100 \quad (1)$$

$$\text{Mol 1,2-PD\%} = \{I_{H5v}/(I_{H5} + I_{H5v})\} \times 100 \quad (2)$$

in which I_{H5} is the integration of the resonance at 0.85–0.94 ppm and I_{H5v} is the integration of the resonance at 1.61–1.70 ppm in the ^{1}H NMR spectrum (see Figures S4 and S6).

$$\text{Mol } \textit{cis}\text{-1,4-PD\%} = \{I_{C1}/(I_{C1} + I_{C1t})\} \times 100 \quad (3)$$

$$\text{Mol } \textit{trans}\text{-1,4-PD\%} = \{I_{C1t}/(I_{C1} + I_{C1t})\} \times 100 \quad (4)$$

in which I_{C1} is the integration of the signals at 35.15 ppm assigned as the methylene carbon of the *cis*-1,4-PD unit and I_{C1t} is the integration of the signals at 40.44 ppm assigned as the methylene carbon of the *trans*-1,4-PD unit in the ^{13}C NMR spectrum (see Figures S5 and S7).

Preparation of isotactic-*cis*-1,4-polyPD-*b*-*cis*-1,4-polyBD diblock copolymer. In the glove box, a predetermined amount of 1,3-butadiene (BD), and 32.0 mg (40 μmol) of $[PhNMe_2H][B(C_6F_5)_4]$ in toluene were introduced sequentially at room temperature in a 30 mL round-bottom glass flask with a stirring bar. A few minutes later, 13 mg (40 μmol) of complex **4** in toluene was added into the flask. After the 1,3-butadiene (BD) was completely consumed, (*E*)-1,3-pentadiene (PD) was added to the reaction mixture. The copolymerization was carried out for a predetermined period of time, and was terminated by addition of 2 mL of methanol. The resulting mixture was poured into methanol (100 mL) to precipitate the polymer product. The polymer was collected by filtration and dried under vacuum at 60 °C to a constant weight.

Table S1. Polymerization of (*E*)-1,3-Pentadiene (PD) by **4**/[$PhMe_2NH$][$B(C_6F_5)_4$][a]

run	cat. [Sc]	T_p (°C)	[PD]/[Sc]	time	yield (%)	microstructure (%)[b] *cis*-1,4-	*trans*-1,4-	1,2-	M_n[c] ($\times 10^4$)	M_w/M_n[c]	T_g[d] (°C)
1	**4**	25	92	5 min	100	72	15	13	2.61	1.27	–50
2	**4**	25	130	5 min	100	71	16	13	3.39	1.27	–50
3	**4**	25	150	5 min	100	70	16	14	4.50	1.27	–52
4	**4**	25	185	5 min	100	70	17	13	5.12	1.26	–49
5	**4**	25	260	5 min	99	71	16	13	6.79	1.26	–50
6	**4**	25	331	5 min	99	71	16	13	10.04	1.26	–50
7	**4**	0	92	5 min	96	85	8	7	2.56	1.28	–55
8	**4**	0	150	5 min	95	85	8	7	5.09	1.28	–55
9	**4**	0	220	5 min	100	85	8	7	9.99	1.30	–55
10	**4**	–20	150	5 min	100	92	4	4	4.24	1.32	–57
11[e]	**4**	–20	150 × 2	10 min × 2	200	92	4	4	9.28	1.37	–57
12	**4**	–40	150	40 min	98	97	1	2	4.46	1.37	–60
13[e]	**4**	–40	150 × 2	50 min × 2	191	97	1	2	6.21	1.37	–59
14	**4**	–60	150	4 h	30	> 99[f]	0	< 1	3.10	1.65	–62[g]
15	**4**	–60	150	24 h	55	> 99[f]	0	< 1	4.45	1.54	–61[g]

[a] Conditions: [Sc], 40 μmol; [$PhMe_2NH$][$B(C_6F_5)_4$], 40 μmol; toluene, 10 mL. [b] Determined by ^1H and ^{13}C NMR. [c] Determined by GPC in THF at 40 °C. [d] Measured by DSC. [e] After polymerization of 150 equiv. of PD for 10 (run 19) or 50 min (run 21), another 150 equiv. of PD was added and the mixture was stirred for a further 10 (run 20) or 50 min (run 22). [f] *mm* > 99% . [g] T_m = 45 °C (run 23) and 43 °C (run 24) were also observed.

Table S2. Polymerization and Block-copolymerization of 1,3-Butadiene (BD) and (*E*)-1,3-Pentadiene (PD) by **4**/[$PhMe_2NH$][$B(C_6F_5)_4$] at -20 °C and -40 °C[a]

run	Temp. (°C)	[PD] /[Sc]	[BD] /[Sc]	*t* (min)	yield (%)	BD cont.[b] (mol%)	*cis*-1,4/*trans*-1,4/1,2[c] (%)	M_n[d] ($\times 10^4$)	M_w/M_n[d]	T_g[e] (°C)
1	-20	0	150	5	100	100	86/4/10	2.61	1.14	-103
2[f]	-20	150	150	10 + 10	200	50	92/4/4[g]	7.17	1.28	-102, -65
3	-40	0	150	120	100	100	87/4/9	1.71	1.22	-105
4[f]	-40	150	150	120 + 120	190	50	97/1/2[g]	3.48	1.39	-104, -70

[a] Conditions: 40 μmol of Sc, 40 μmol of [$PhMe_2NH$][$B(C_6F_5)_4$], 10 mL of toluene. [b] Calculated from yield. [c] Determined by ^1H and ^{13}C NMR. [d] Determined by GPC in THF at 45 °C. [e] Measured by DSC. [f] After polymerization of 150 equiv. of BD for 10 min or 120 min, another 150 equiv. of PD was added and the mixture was stirred for a further 10 min or 120 min. [g] Microstructure for PPD. Microstructure for PBD: *cis*-1,4-/*trans*-1,4-/1,2 = 86/4/10.

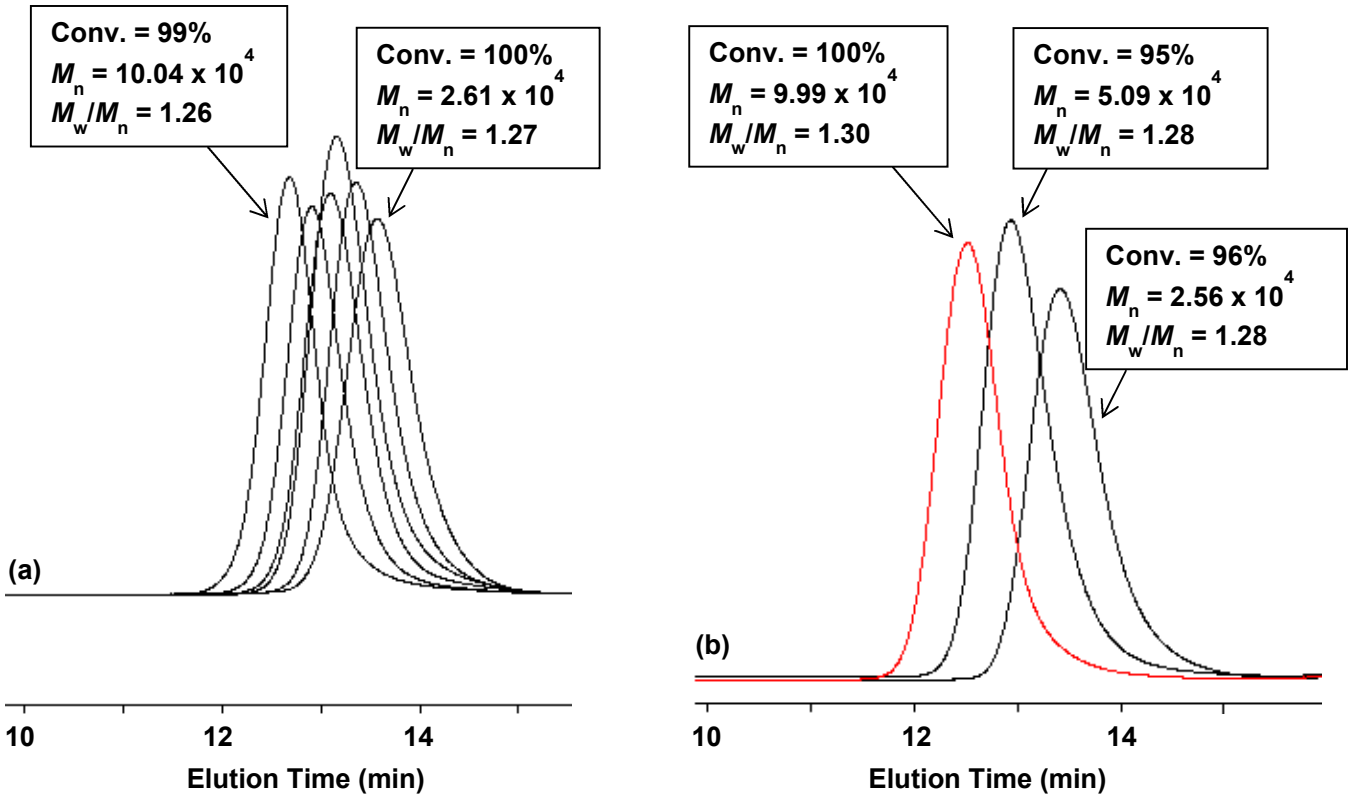


Figure S1. GPC curves of polypentadienes obtained by **4**/[$PhNMe_2H$][$B(C_6F_5)_4$] at 25 °C (a) (Tables S1, runs 1-6) and 0 °C (b) (Tables S1, runs 7-9).

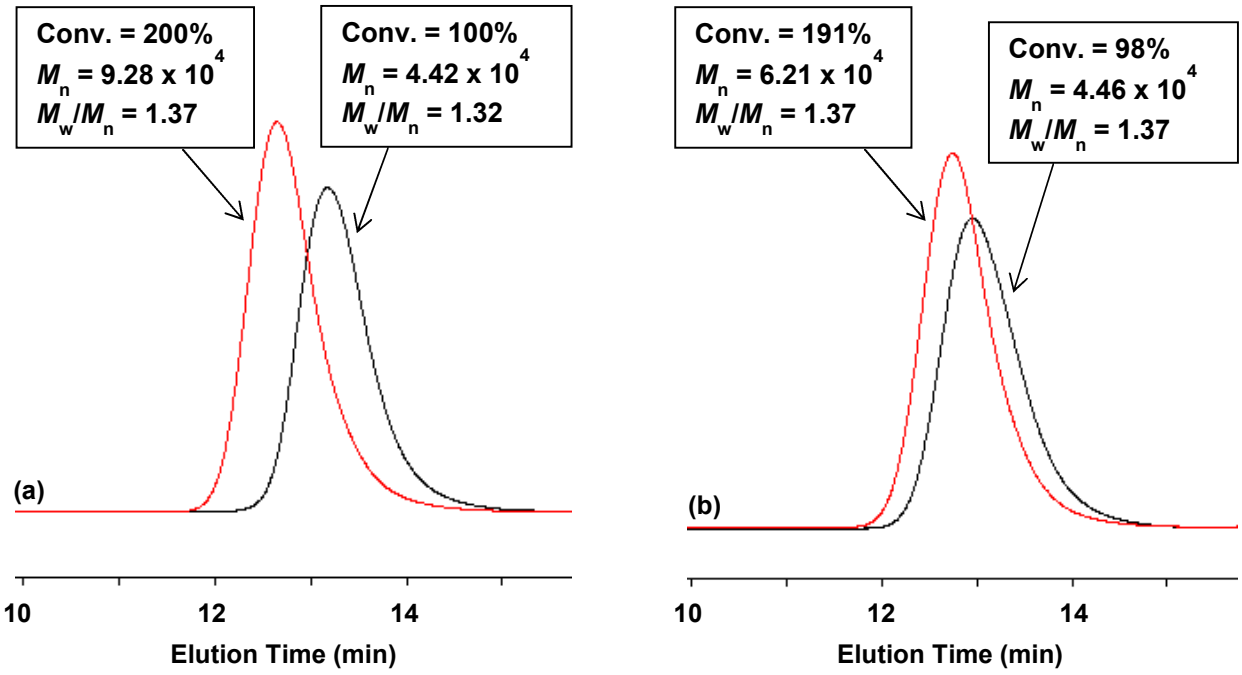


Figure S2. GPC curves of polypentadienes obtained by **4**/[$PhNMe_2H$][$B(C_6F_5)_4$] at -20 °C (a) (Tables S1, runs 10, 11) and -40 °C (b) (Table S1, runs 12, 13).

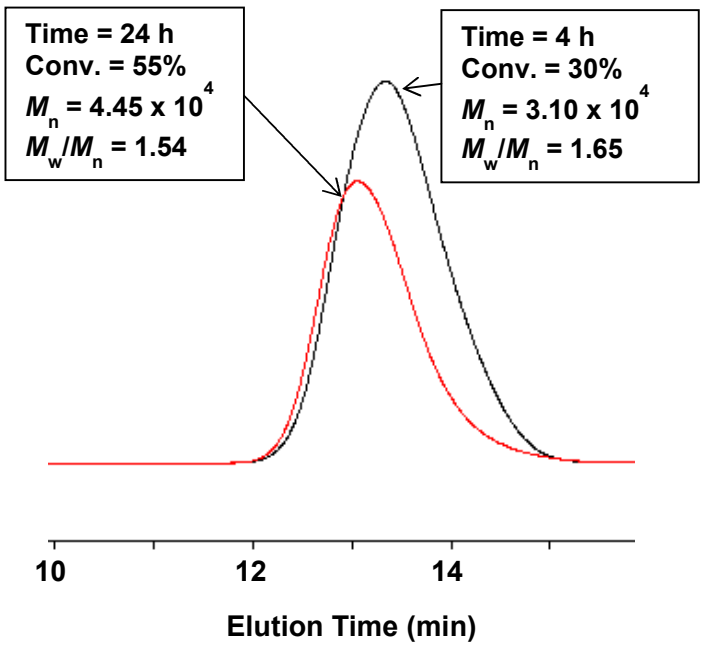


Figure S3. GPC curves of polypentadienes obtained by **4**/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] at -60 °C (Table S1, runs 14, 15).

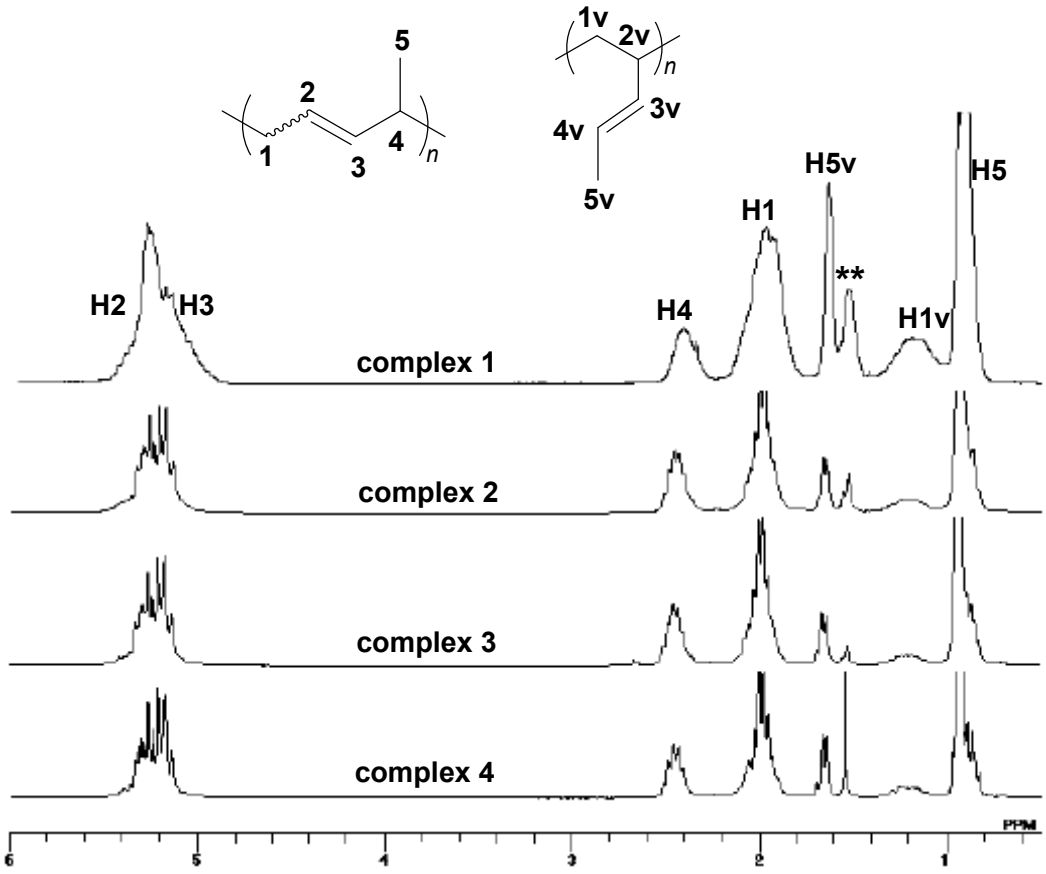


Figure S4. ^{1}H NMR spectra of polypentadienes obtained by **1-4**/[$PhNMe_2H$][$B(C_6F_5)_4$] at 25 °C (Table 1, runs 1-4). (**: H_2O)

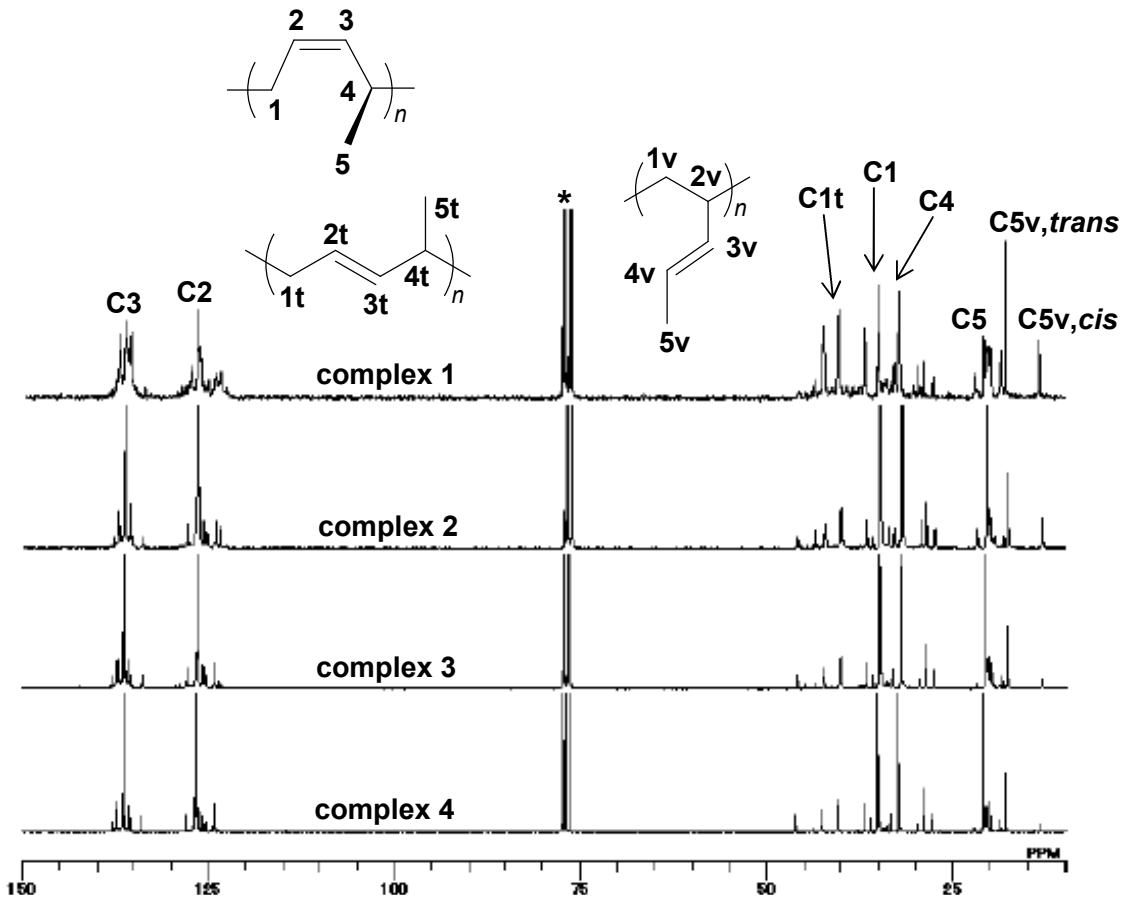


Figure S5. ^{13}C NMR spectra of polypentadienes obtained with **1**-**4**/[$PhNMe_2H$][$B(C_6F_5)_4$] at 25 °C (Table 1, runs 1-4). (*: $CDCl_3$)

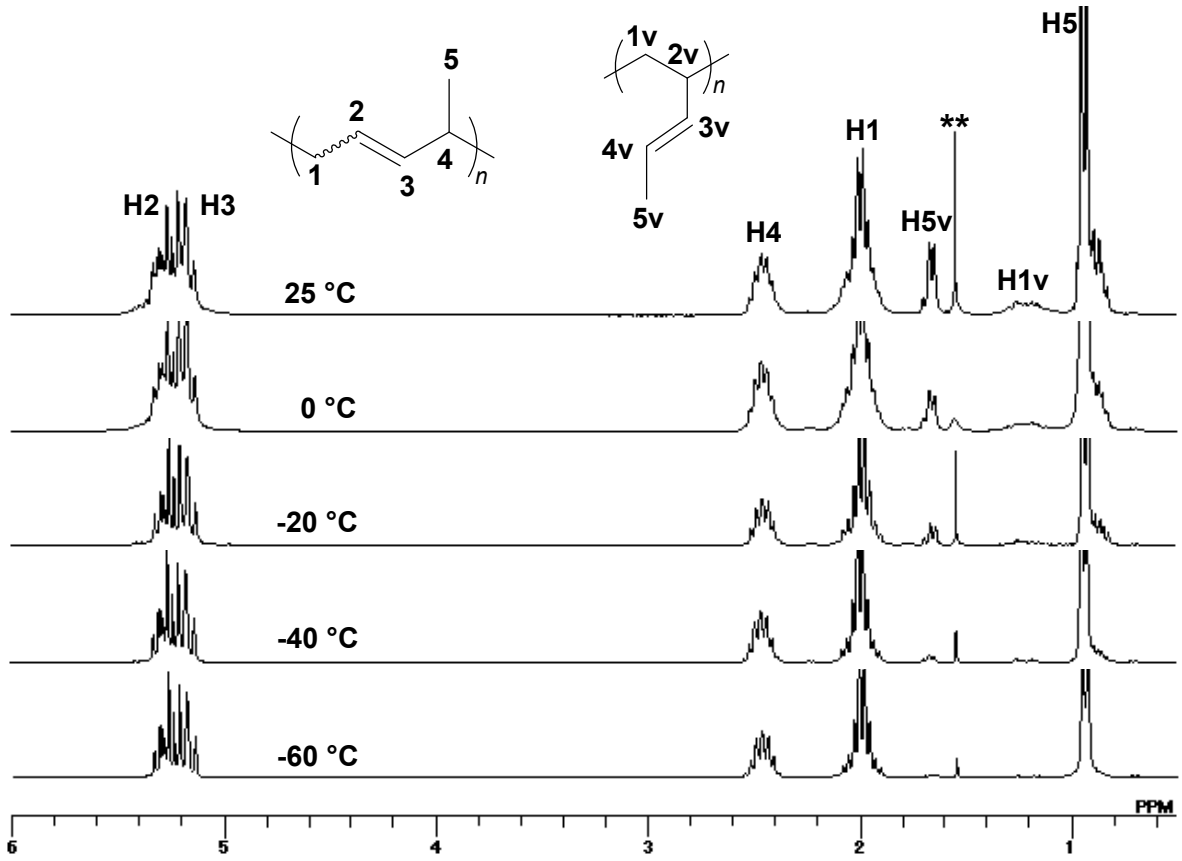


Figure S6. ^{1}H NMR spectra of polypentadienes obtained by **4**/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (Table S1, runs 3, 8, 10, 12, 14). (**: H_2O)

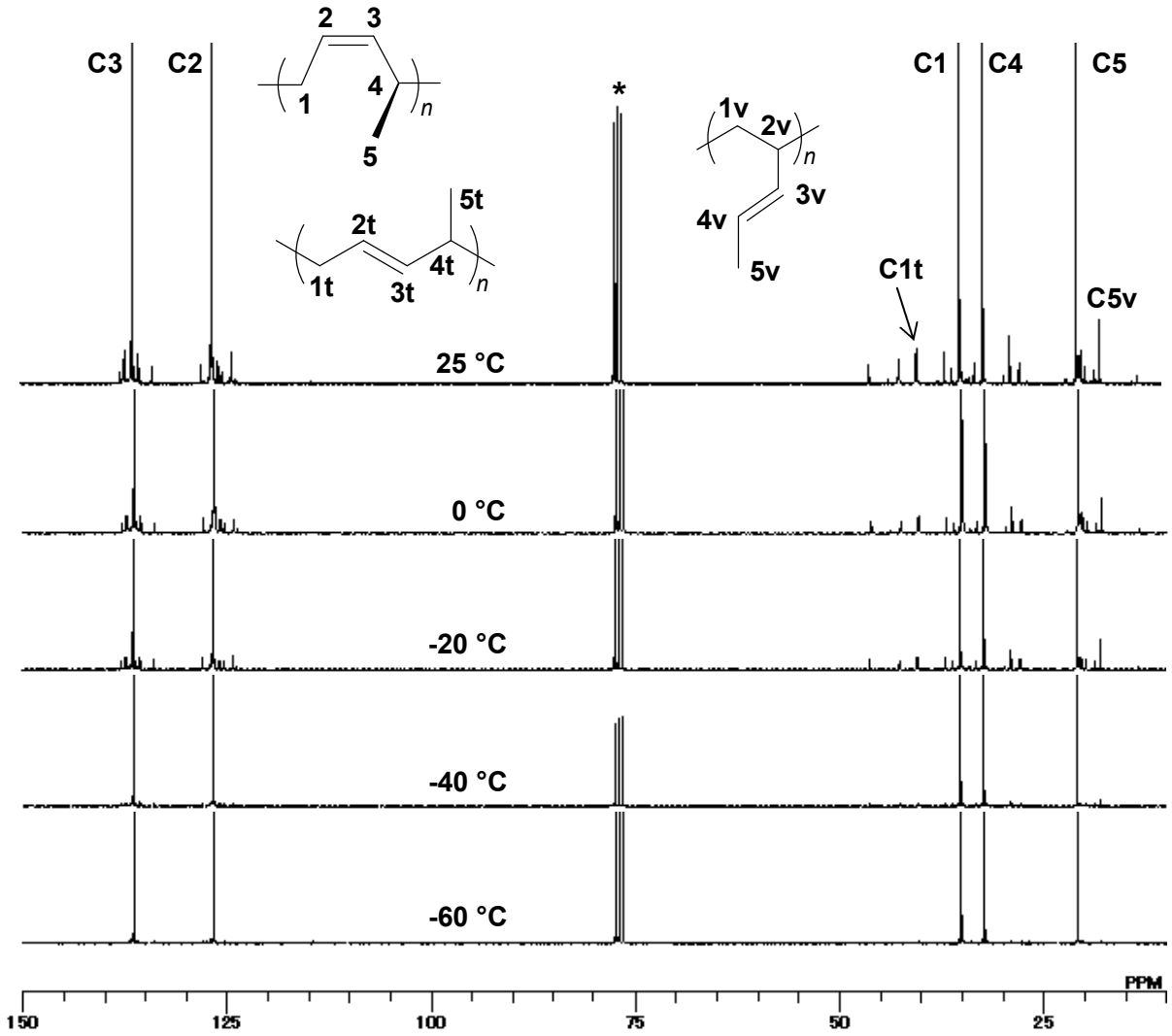


Figure S7. ^{13}C NMR spectra of polypentadienes obtained by **4**/[$PhNMe_2H$][$B(C_6F_5)_4$] (Table S1, runs 3, 8, 10, 12, 14). (*: $CDCl_3$)

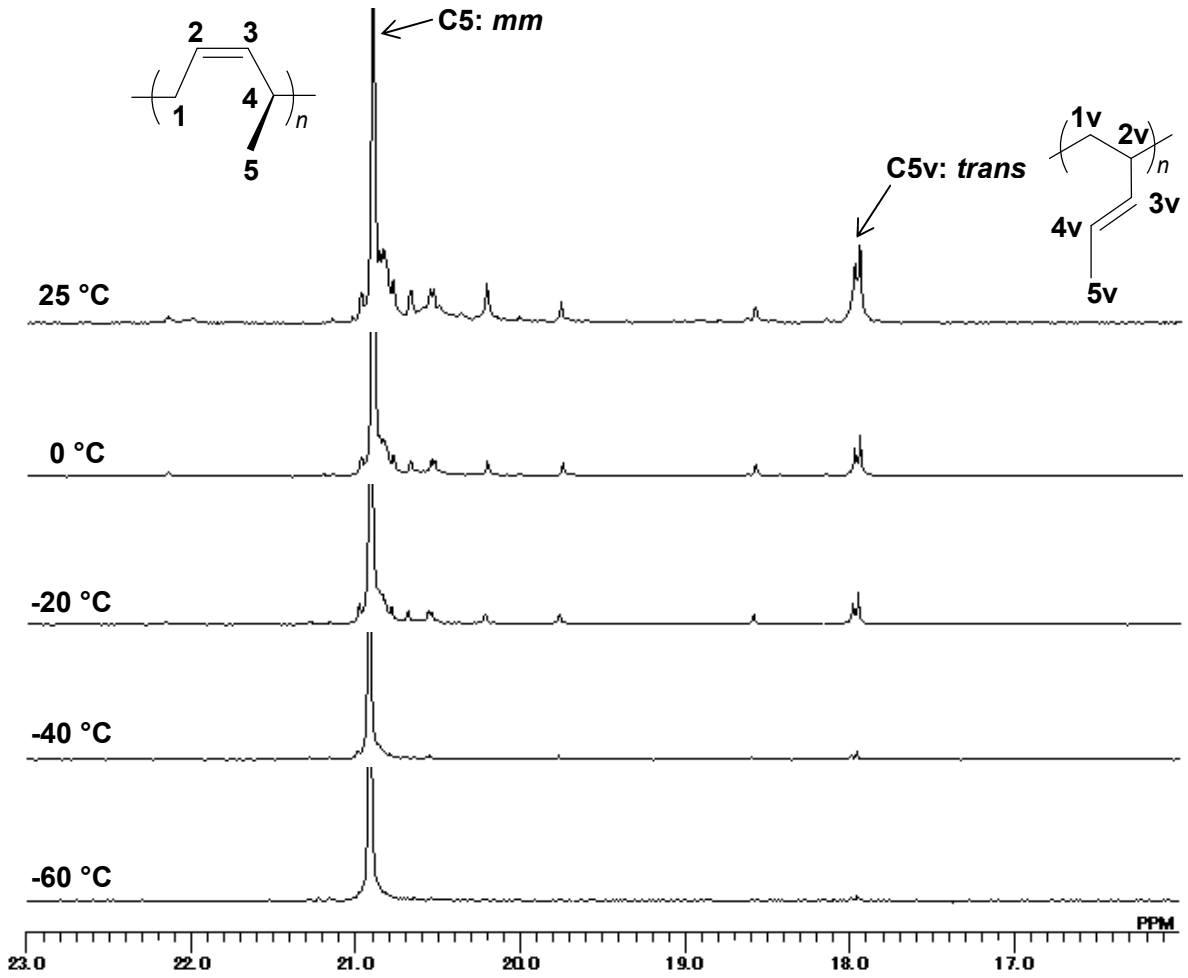
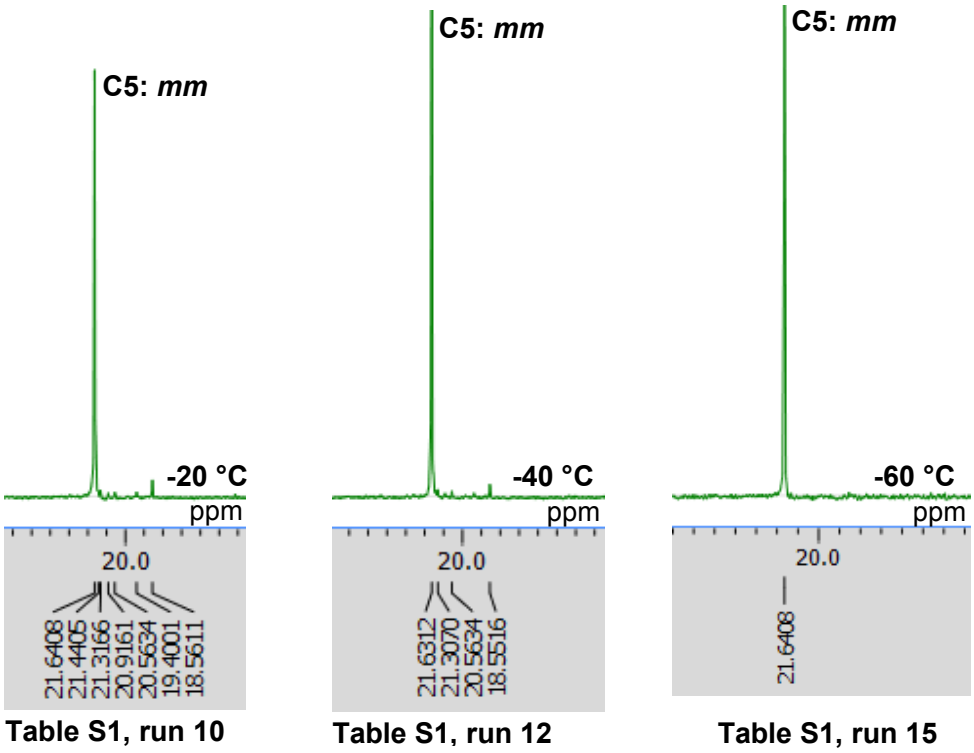


Figure S8. ^{13}C NMR spectra of the aliphatic region of polypentadienes obtained by **4**/[$PhNMe_2H$][$B(C_6F_5)_4$] (Table S1, runs 3, 8, 10, 12, 14).



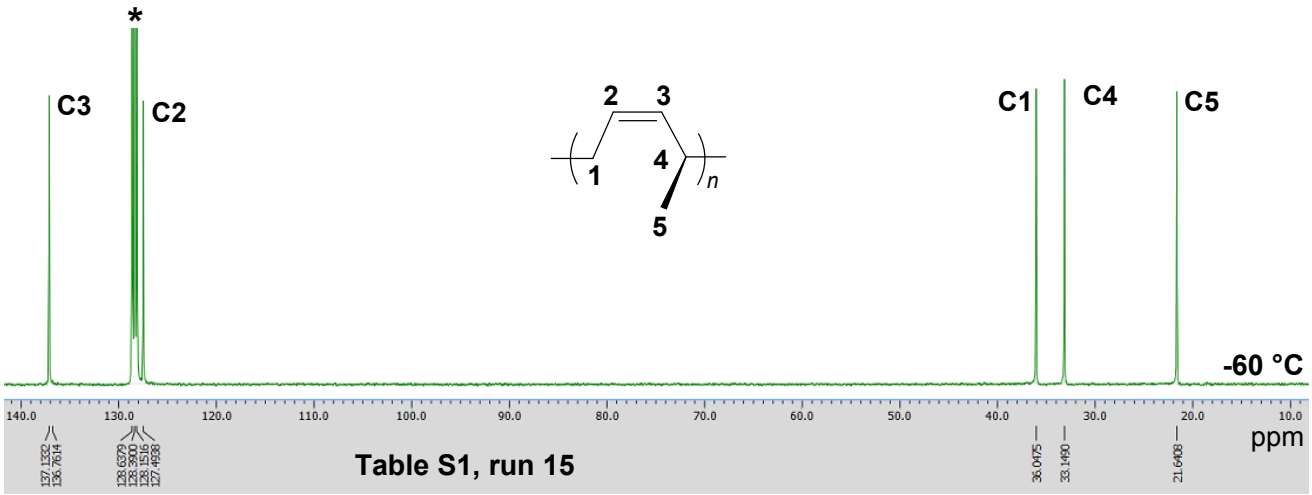


Figure S9. ^{13}C NMR spectra (*: C_6D_6) of polypentadiene obtained by **4**/[PhNMe$_2$H][B(C_6F_5)$_4$] (Table S1). The peak at 21.641 ppm (-20 °C), 21.631 ppm (-40 °C) and 21.641 ppm (-60 °C) are attributable to "*mm*" triads (see *J. Organomet. Chem.* **1993**, *451*, 67, *mm*; δ = 21.632 ppm, *mr*; δ = 21.490 ppm).

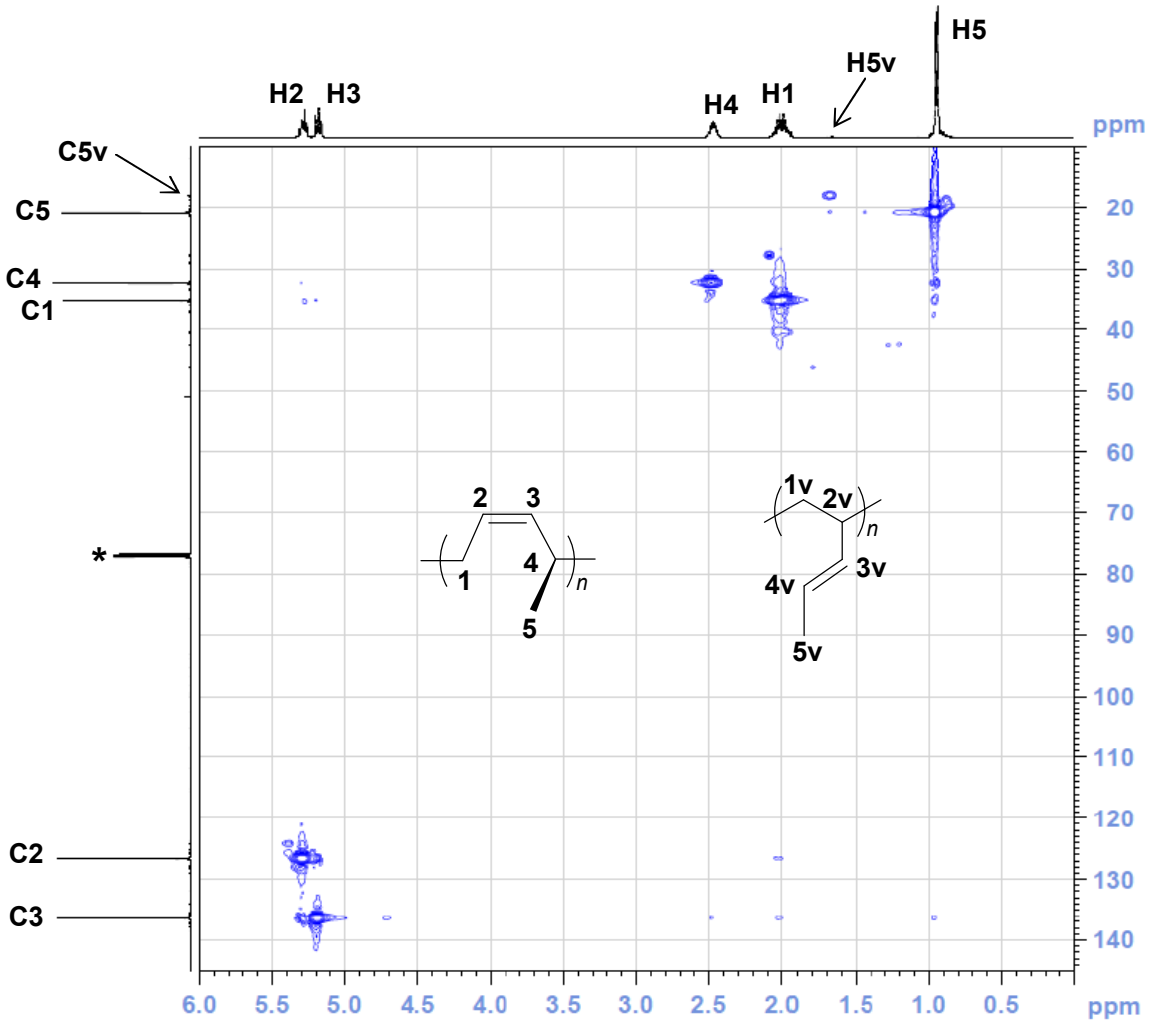


Figure S10. ^{1}H-^{13}C HMQC spectrum of polypentadiene obtained at -40 °C by **4**/[$PhNMe_2H$][$B(C_6F_5)_4$] (Table S1, run 12). (*: $CDCl_3$)

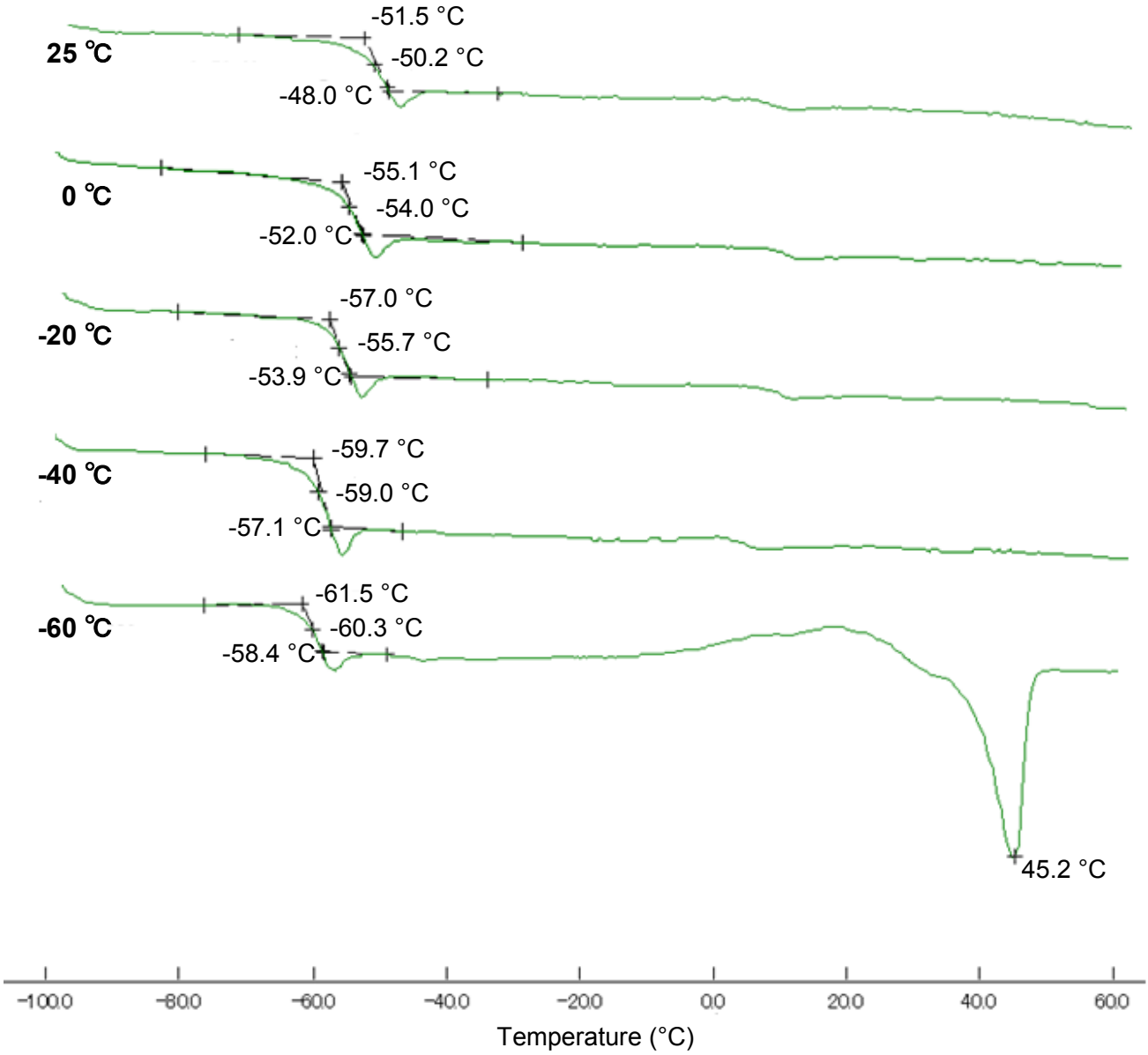


Figure S11. DSC curves of polypentadienes obtained by **4**/[$PhNMe_2H$][$B(C_6F_5)_4$] (Table S1, Table S1, runs 3, 8, 10, 12, 14).

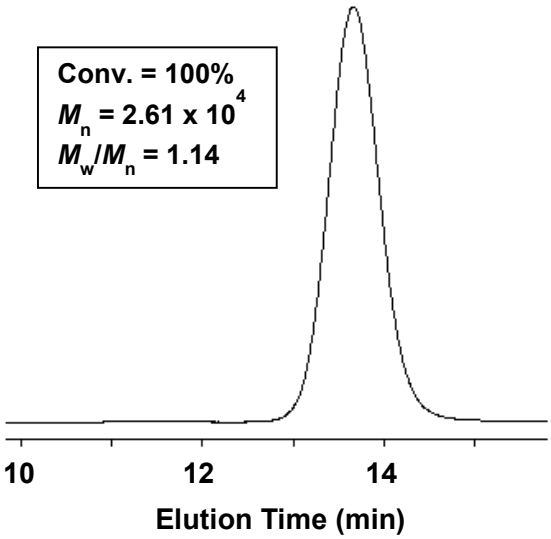


Figure S12. GPC curves of polybutadiene obtained at -20 °C (Table S2, run 1).

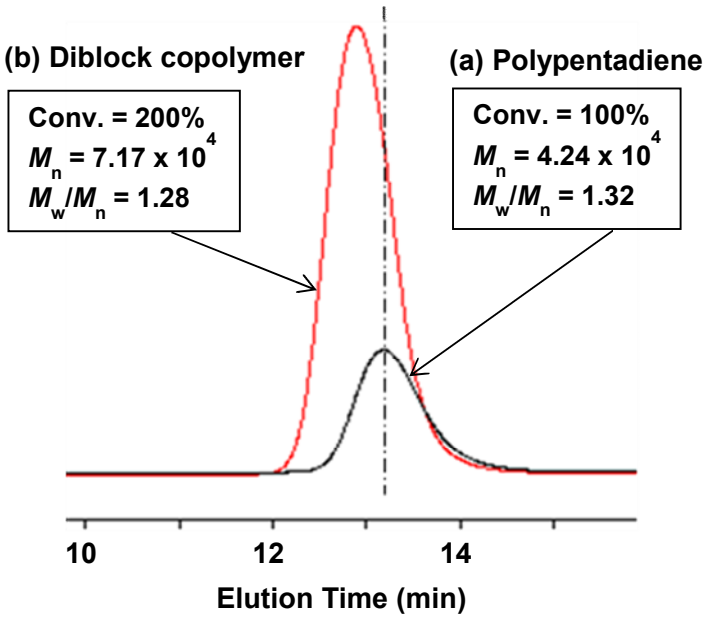


Figure S13. GPC curves of polypentadiene (a) and pentadiene-butadiene diblock copolymer (b) obtained at -20 °C (Table S1 run 10 and Table S2, run 4).

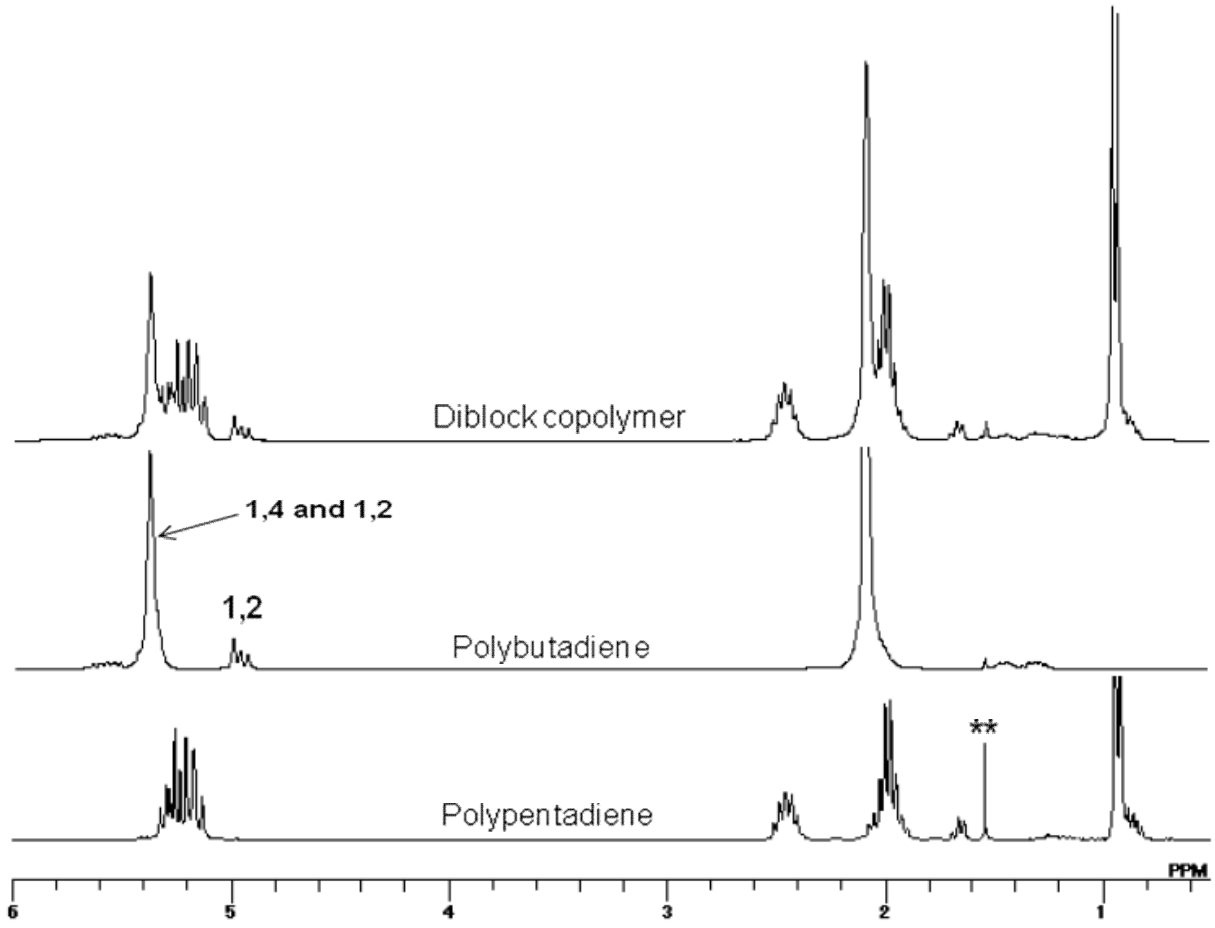


Figure S14. ^{1}H NMR spectra of pentadiene-butadiene diblock copolymer, polybutadiene and polypentadiene obtained by **4**/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] at -20 °C (Table S1, run 10 and Table S2, runs 1, 2). (**: H_2O)

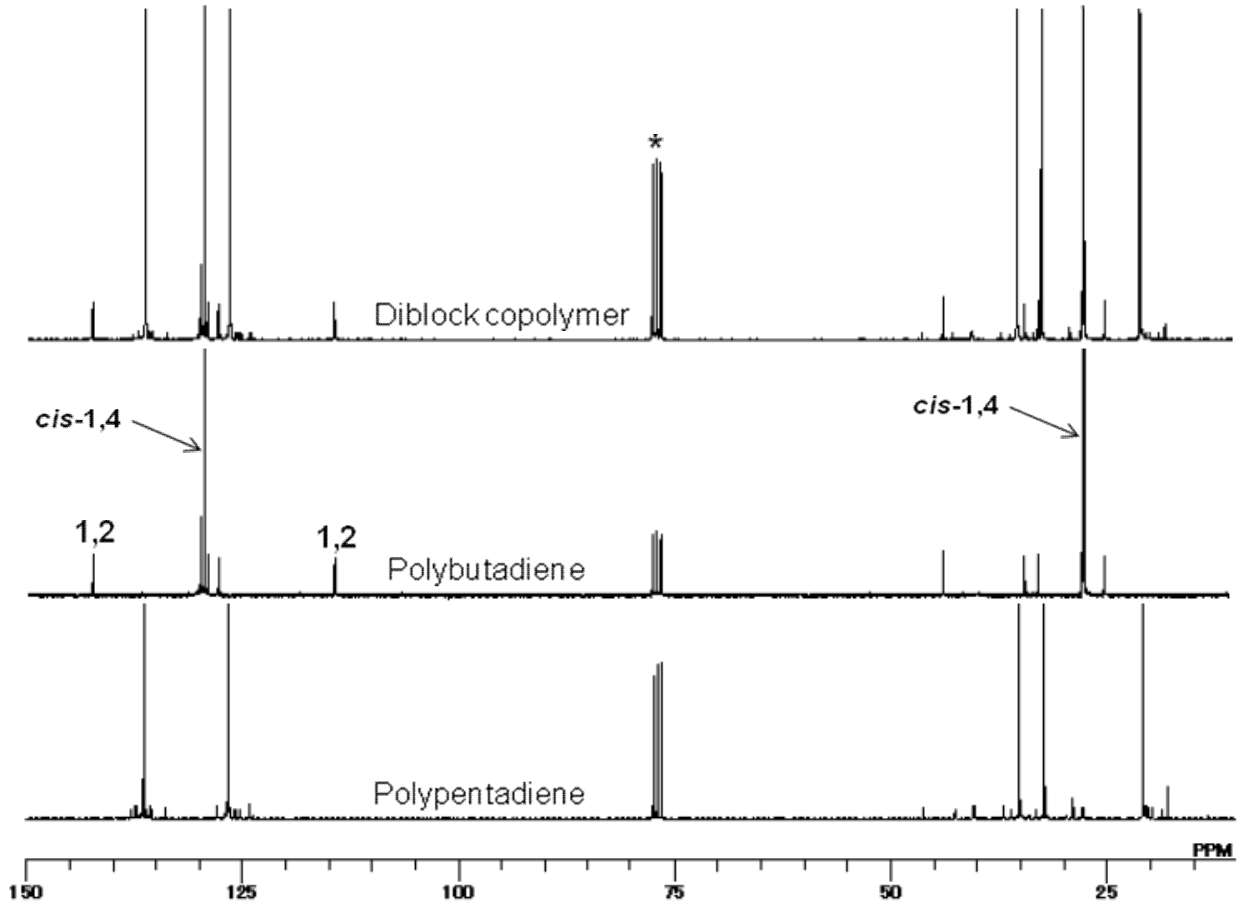


Figure S15. ^{13}C NMR spectra of pentadiene-butadiene diblock copolymer, polybutadiene and polypentadiene obtained by **4**/[$PhNMe_2H$][$B(C_6F_5)_4$] at -20 °C (Table S1, run 10 and Table S2, runs 1, 2). (*: $CDCl_3$)

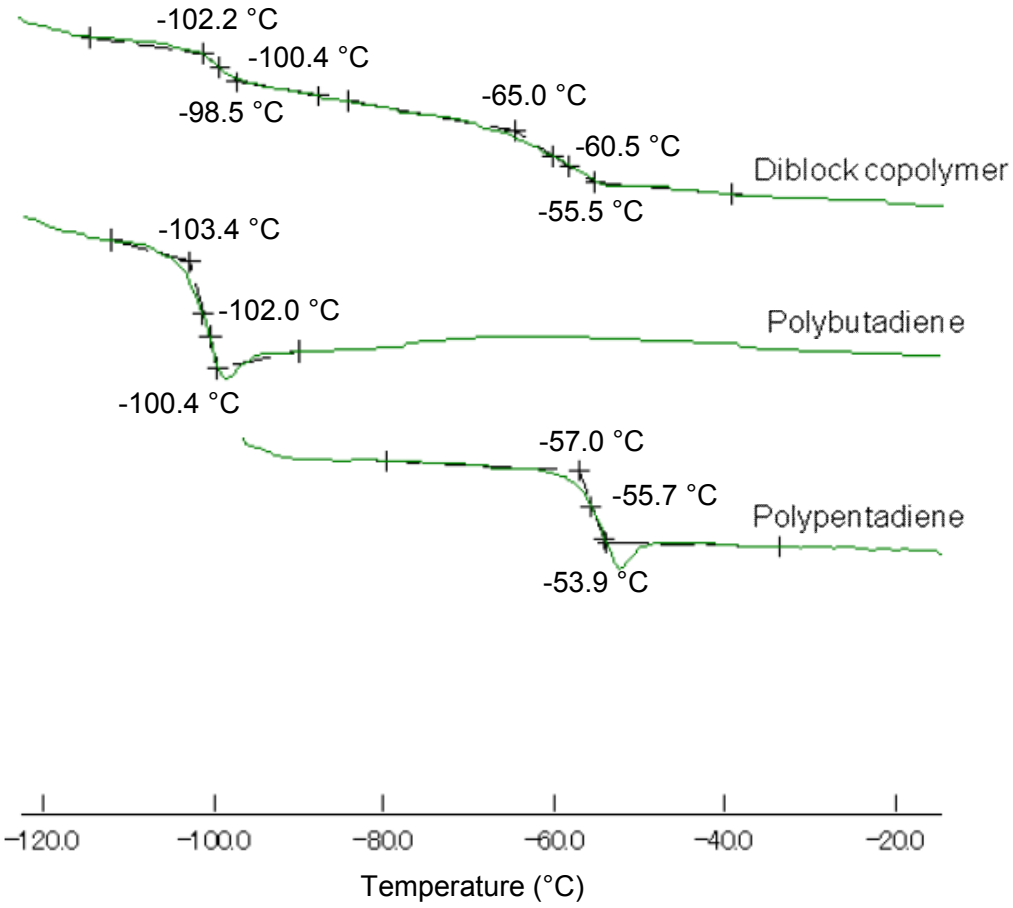


Figure S16. DSC curves of pentadiene-butadiene diblock copolymer, polybutadiene and polypentadiene obtained by **4**/[$PhNMe_2H$][$B(C_6F_5)_4$] at -20 °C (Table S1, run 10 and Table S2, runs 1, 2).

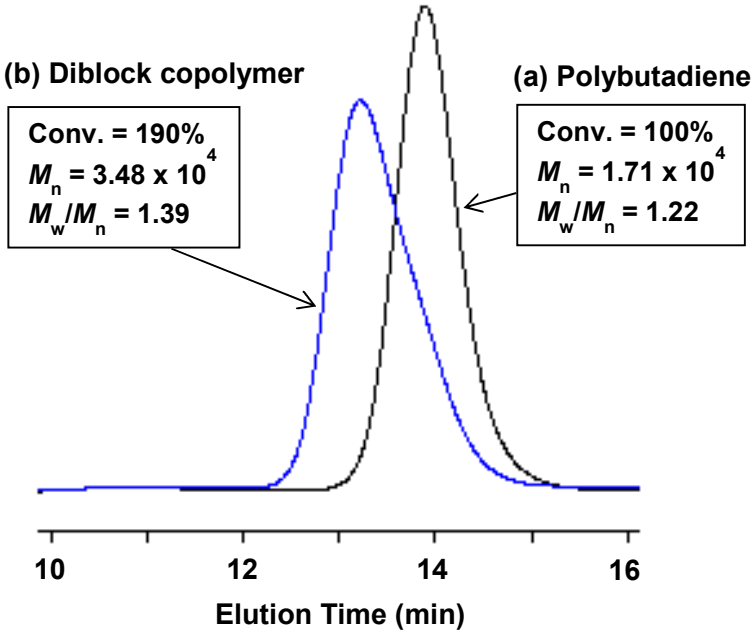


Figure S17. GPC curves of polypentadiene (a) and pentadiene-butadiene diblock copolymer (b) obtained at -40 °C (Table S2, runs 3, 4).

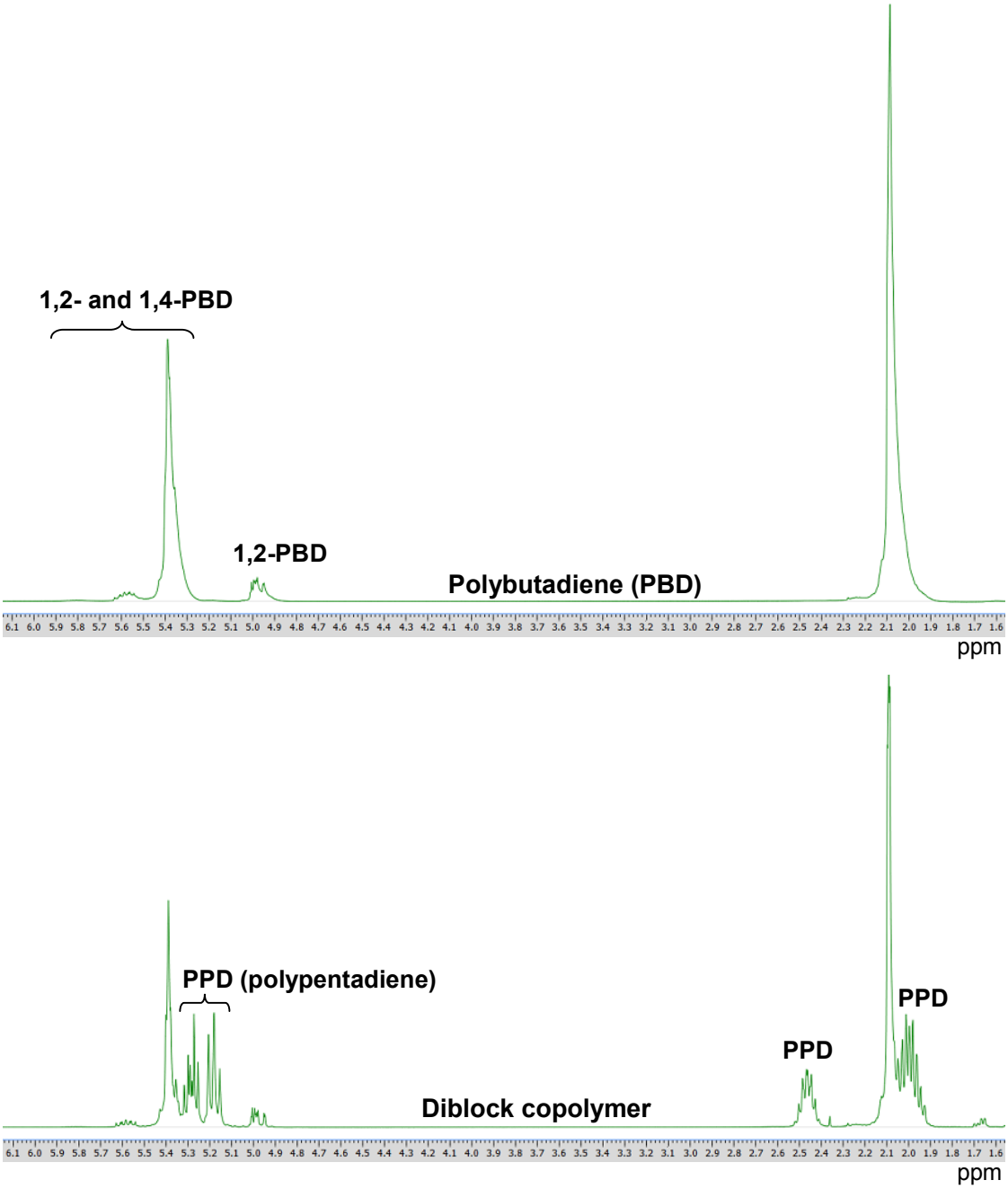


Figure S18. ^{1}H NMR spectra of polybutadiene and pentadiene-butadiene diblock copolymer obtained by **4**/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] at -40 °C (Table S2, runs 3, 4).

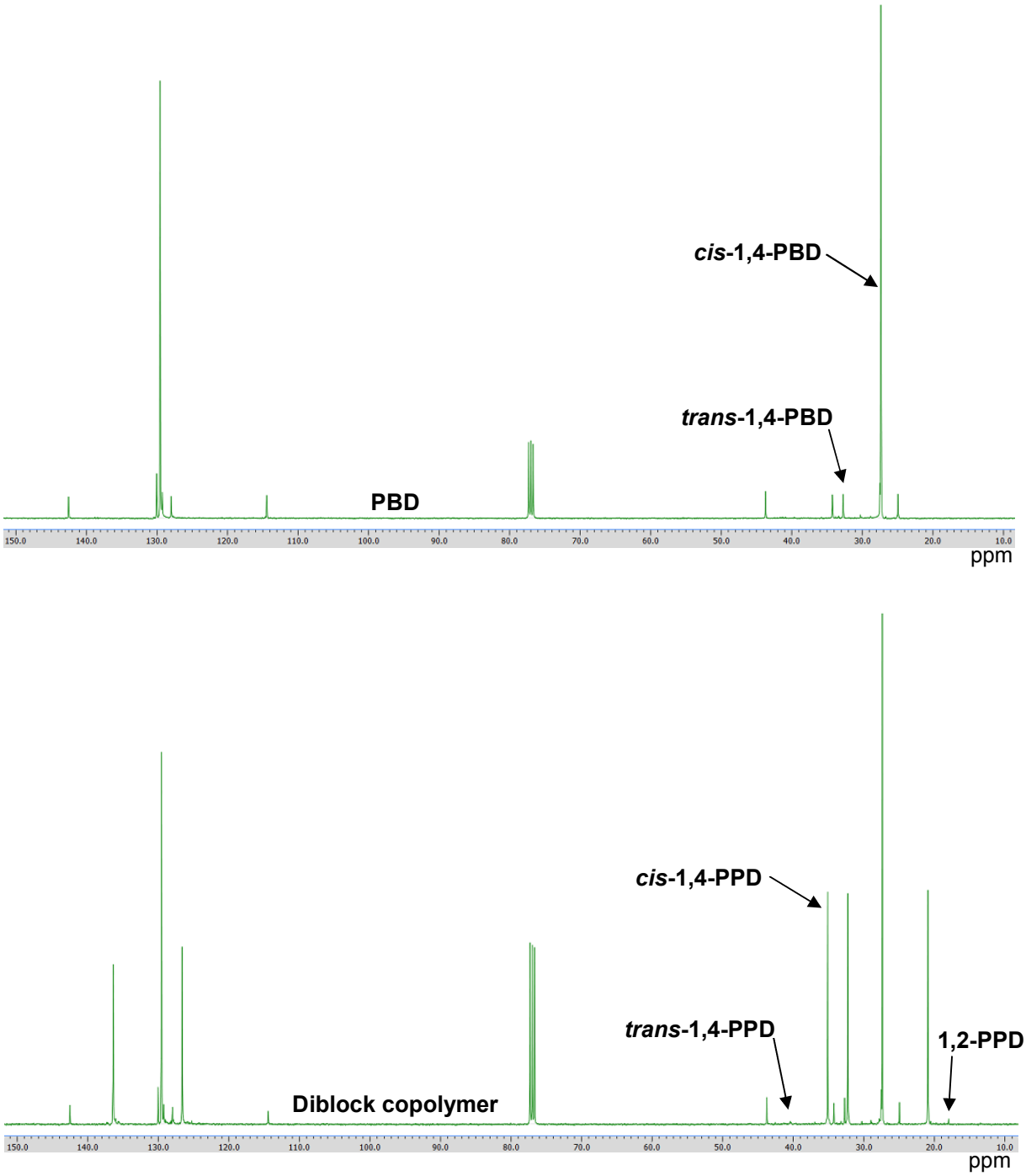


Figure S19. ^{13}C NMR spectra of polybutadiene and pentadiene-butadiene diblock copolymer obtained by **4**/[$PhNMe_2H$][$B(C_6F_5)_4$] at -40 °C (Table S2, runs 3, 4).

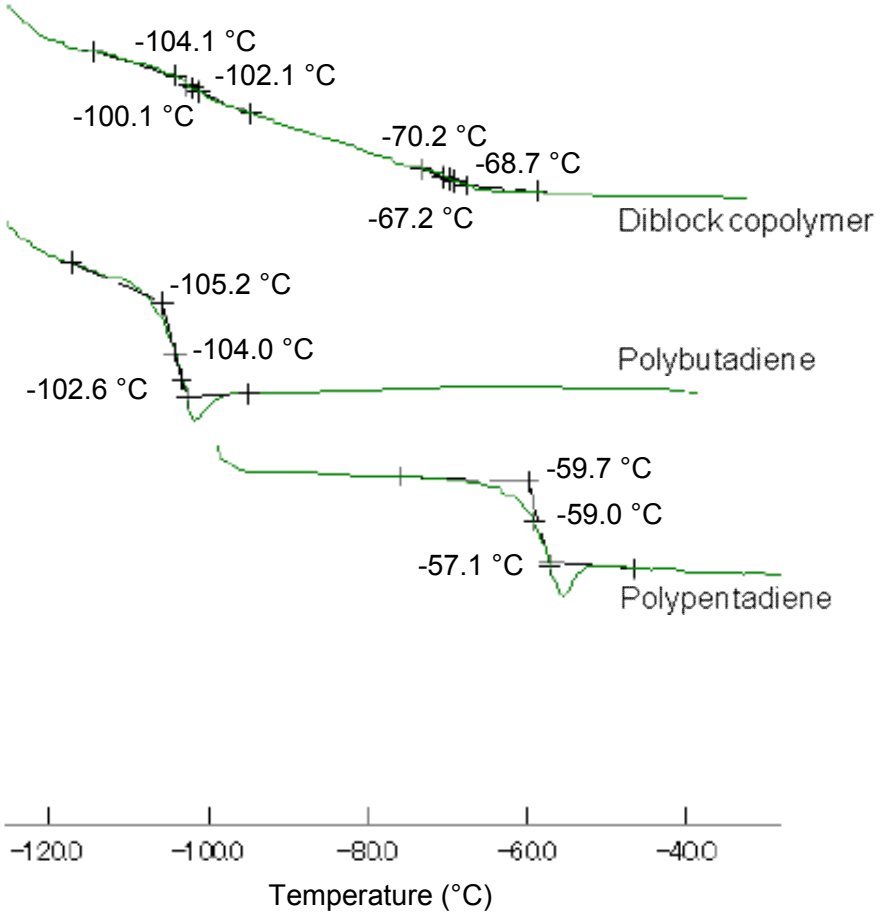
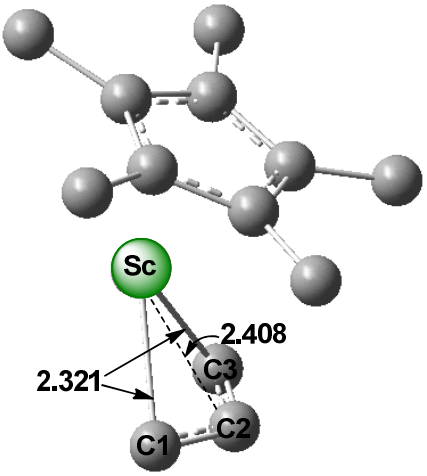


Figure S20. DSC curves of pentadiene-butadiene diblock copolymer, polybutadiene and polypentadiene obtained by **4**/[$PhNMe_2H$][$B(C_6F_5)_4$] at -40 °C (Table S1, run 12 and Table S2, runs 3, 4).

Computational details. All calculations were performed with Gaussian 09 program.[1] The DFT method of B3PW91[2] was used for geometry optimizations. The 6-31G* basis set was used for C and H atoms, and the Sc atom was treated by the Stuttgart/Dresden effective core potential (ECP) and the associated basis set.[3] In the Stuttgart/Dresden ECP used in this study, the most inner 10 electrons of Sc are included in the core. The 11 valence electrons of Sc were treated by the optimized basis set, viz. (8s7p6d1f)/[6s5p3d1f]. Such a basis set contains one f-polarization function with an exponent of 0.27. Each optimized structure was analyzed by harmonic vibrational frequencies at the same level of theory to characterize the minima (Nimag = 0) and the transition states (Nimag = 1). The C_5Me_5 ligand was used as a model of $C_5Me_4SiMe_3$ to save computational time. Such a strategy was successfully adopted in our previous work.[4]

1. Cationic Active Species The cationic scandium allyl complex $[(\eta^5\text{-}C_5Me_5)Sc(\eta^3\text{-}C_3H_5)]^+$ has been optimized to model the initial active species (Figure S21). The Sc—C(allyl) distances are 2.321 Å for Sc–C1 and Sc—C3) bonds and 2.408 Å Sc–C2 contacts.



$[(\eta^5\text{–}C_5Me_5)Sc(\eta^3\text{-}C_3H_5)]^+$

Figure S21. Optimized structure (distance in Å) of cationic half-sandwich scandium alkyl species.

2. Chain initiation The computed free energies (in kcal/mol) of stationary points possibly involved in the chain initiation stage are shown in Table S3. (s-*trans*-1,4-*supine* represents insertion of the *E*-1,3-pentadiene with s-*trans* coordination mode into Sc-allyl bond to form a π-allyl intermediate with *supine* form). Structures of four inserted intermediates are shown in Figure S22. Among these pathways, s-*cis*-1,4-*prone* showed a lowest energy barrier (8.3 kcal/mol) to give *cis*-1,4 pentenyl unit which is consistent with the fact that the *cis*-1,4-selectivity was dominant during the polymerization. .

Table S3. The computed free energies (Δ*G*, kcal/mol) relative to the separate active species and the monomer

Insertion modes	Δ*G* (kcal/mol)		
	Pre-reaction complex (C)	**Transition state (TS)**	**Insertion product (P)**
s-trans-1,4-*supine*	–11.5(**C_{ss}**)	5.1(**TS_{ss}**)	–18.1(**P_{ss}**)
s-trans-1,4-*prone*	–12.2(**C_{sp}**)	12.5(**TS_{sp}**)	–12.7(**P_{sp}**)
s-cis-1,4-*supine*	-7.4(**C_{as}**)	10.0(**TS_{as}**)	–12.4(**P_{as}**)
s-cis-1,4-*prone*	-8.1(**C_{ap}**)	0.2(**TS_{ap}**)	–15.7(**P_{ap}**)

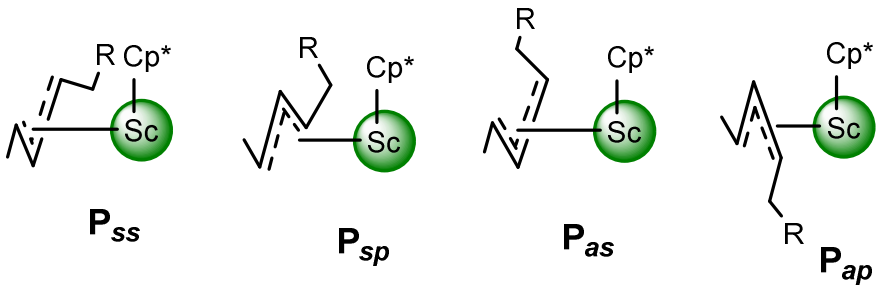


Figure S22. Four structures of allyl inserted intermediates, *syn-supine* ($\mathbf{P_{ss}}$), *syn-prone* ($\mathbf{P_{sp}}$), *anti-supine* ($\mathbf{P_{as}}$), and *anti-prone* ($\mathbf{P_{ap}}$) are shown.

3. Isotacticity The critical factor for the formation of tactic 1,4-polymers is the mutual orientation of the butenyl and butadiene part.[5] Based on the more accessible chain propagation species $\mathbf{P_{ap}}$, the anti(*prone)*-s-*cis*(*prone)* and anti(*prone)*-s-*cis*(*supine)* polymerization processes (Figure S23) have been investigated computationally as indicated by Table S4. The anti(*prone)*-s-*cis*(*prone)* process which gives isotactic *cis*-1,4-poly(PD), is more favorable both kinetically and thermodynamically than anti(*prone)*-s-*cis*(*supine)* process to give syndiotactic *cis*-1,4-poly(PD), probably because of the steric repulsion between Cp* and methyl of pentadiene in $\mathbf{'TS_{ac}}$ (Figure S24).

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Table S4. The Computed free energies for insertion of (*E*)-PD into the Sc–C bond of $\mathbf{P_{ap}}$ in a s-*cis*(*supine)* and s-*cis*(*prone*) manner (energies are relative to the energy sum of $\mathbf{P_{ap}}$ and (*E*)-PD).

Insertion modes	ΔG (kcal/mol)		
	C	**TS**	**P**
anti-s-cis(*prone*)	4.2($\mathbf{C_{ac}}$)	8.8($\mathbf{TS_{ac}}$)	-8.9($\mathbf{P_{ac}}$)
anti-s-cis(*supine*)	0.6($\mathbf{'C_{ac}}$)	23.8($\mathbf{'TS_{ac}}$)	-4.9($\mathbf{'P_{ac}}$)

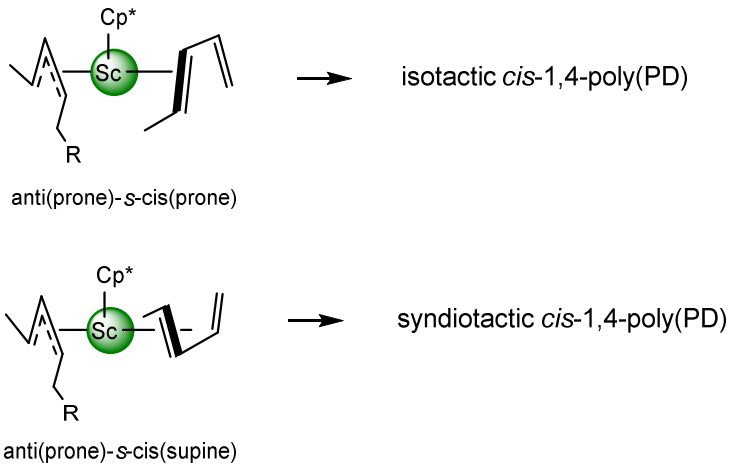

Figure S23. Formation of iso- and syndiotactic-*cis*-1,4-polymer units.

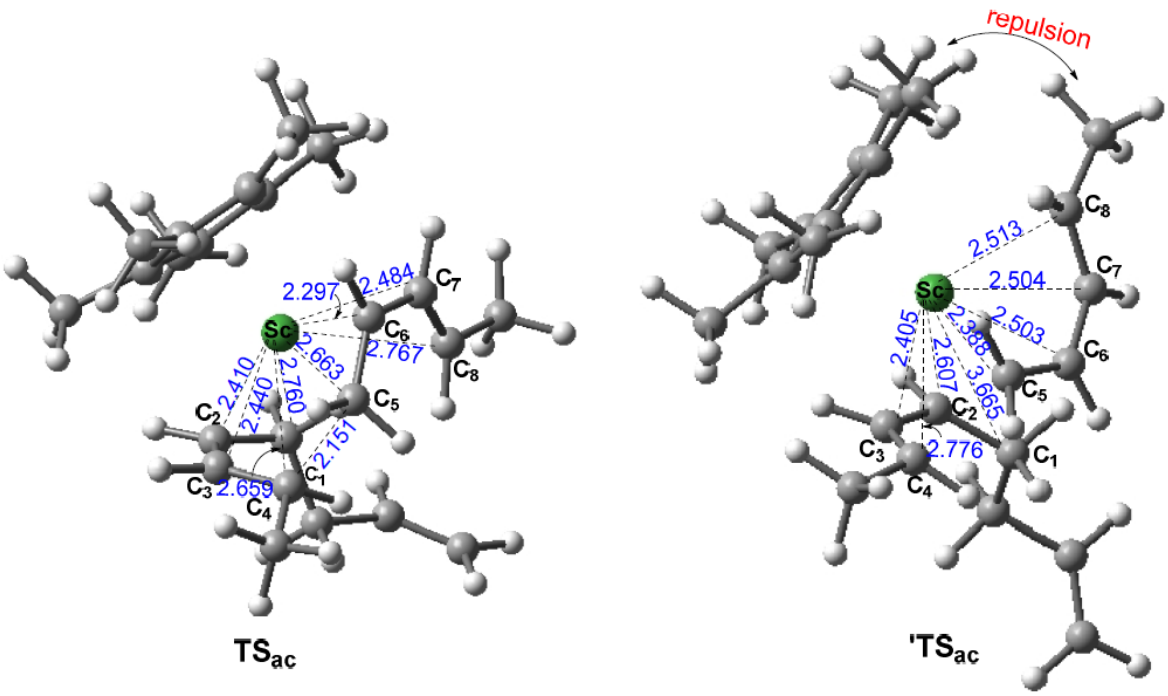

Figure S24. Structures (distances in Å) for $\mathbf{TS_{ac}}$ and $\mathbf{'TS_{ac}}$.

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Table S5. Optimized artesian coordinates (Å) and zero-point energy corrected energies (a.u.) of the transition states as well as their imaginary frequencies (cm^{-1})

Atom	X	Y	Z
TS_{ss}, -749.106501581, ***i*324**			
Sc	-0.23812600	0.44807600	-0.26966000
C	-0.41479700	3.11157100	-0.34265300
H	-1.33345700	3.27040400	-0.91081100
H	-0.12865800	3.98958100	0.23114100
C	0.65314000	2.56302400	-1.13910600
C	0.46516900	1.69643600	-2.19079800
H	-0.52790500	1.59318000	-2.64699800
H	1.29824500	1.32048800	-2.77360700
C	1.44527800	-0.35533100	1.31222300
C	2.09933400	-0.22035700	0.05107000
C	1.50909500	-1.15156900	-0.85402200
C	0.50462000	-1.87831700	-0.14618400
C	0.47467800	-1.39586900	1.19829300
C	3.30553400	0.62848200	-0.22703600
H	4.22119700	0.04489100	-0.06482100
H	3.36693300	1.49708700	0.43657200
H	3.34150300	0.98800300	-1.26096100
C	1.96655900	-1.45719000	-2.25146100
H	2.56394400	-2.37836500	-2.26390800
H	2.60006100	-0.66519200	-2.66034800
H	1.13343400	-1.61324800	-2.94681000
C	-0.21876700	-3.07919500	-0.68740900
H	0.44645500	-3.95281500	-0.68172500
H	-0.54678700	-2.94239800	-1.72410000
H	-1.09440800	-3.34730700	-0.08925200
C	-0.27242200	-2.01838800	2.34170100
H	-1.23918500	-2.43989100	2.04677600
H	-0.45070900	-1.31492000	3.16174900
H	0.31305400	-2.84576500	2.76394300
H	1.67362400	2.74475100	-0.80234200
C	1.80932100	0.36757800	2.57820700
H	0.95147500	0.49160300	3.24764500
H	2.56868200	-0.19373000	3.13836100
H	2.22864600	1.36063400	2.38600100
C	-2.86016600	-0.73289000	-0.15948400
C	-2.67943000	0.55576800	0.25037400
H	-2.41957800	-1.53155700	0.43704300
H	-3.16598700	1.34118200	-0.33751600
C	-1.77549400	0.99429800	1.29266900
C	-1.34710900	2.34991900	1.31288900
H	-0.66750400	2.63144700	2.11489600
H	-2.08984200	3.11631300	1.10337300
H	-1.47520900	0.31208100	2.08163200
C	-3.75745400	-1.15270500	-1.27770900
H	-3.25607000	-1.85194400	-1.95780000
H	-4.63023400	-1.68675300	-0.87792400
H	-4.12361600	-0.29892800	-1.85673200

TS_{sp}, -749.094380112, ***i*342**

Sc	-0.06524300	0.53246600	-0.25457100
C	1.53038300	2.64699400	0.17733300
H	1.25588300	3.68555300	0.01224600
H	2.29321900	2.52420100	0.94306700
C	1.72915200	1.91811600	-1.04557400
C	0.86077200	1.96434800	-2.11501700
H	0.13246100	2.76682100	-2.21489600
H	1.05075400	1.36770600	-3.00501700
C	0.57402600	-1.08071200	1.44464600
C	1.73680400	-0.87713400	0.64044300
C	1.44608000	-1.35065200	-0.67456100
C	0.10701800	-1.85290900	-0.68097800
C	-0.41968100	-1.71461800	0.63689000
C	3.07815800	-0.43618500	1.14942800
H	3.65336300	-1.30576700	1.49330200
H	2.99722200	0.24589600	2.00131800
H	3.68625600	0.05543000	0.38301300
C	2.41693800	-1.46963200	-1.81365100
H	2.85831800	-2.47487900	-1.82822700
H	3.25061500	-0.76511600	-1.73282300
H	1.94238800	-1.32024600	-2.78939900
C	-0.56180900	-2.53189200	-1.84290400
H	-0.28435300	-3.59352100	-1.88172200
H	-0.26998800	-2.09535600	-2.80447200
H	-1.65309200	-2.48956500	-1.77482800
C	-1.70095400	-2.30150400	1.14780200
H	-2.41978800	-2.48752000	0.34675400
H	-2.18598200	-1.67341400	1.90301900
H	-1.49892900	-3.26808900	1.62834400
H	2.52980400	1.18255200	-1.06934400
C	0.47167100	-0.84995900	2.92667400
H	-0.54958800	-0.61144000	3.24389900
H	0.76845300	-1.75279200	3.47659800
H	1.12721900	-0.04310500	3.27008400
C	-2.91100000	0.72288400	-0.64995500
C	-2.27601800	1.24883600	0.44144400
H	-2.72626600	1.19689500	-1.62072600
H	-2.43264800	0.76217900	1.40863600
C	-1.38170500	2.38441400	0.38438700
C	-0.27716700	2.54624400	1.25120400
H	-0.00669600	3.52877200	1.62075700
H	-0.12819700	1.78063800	2.02399800
H	-1.59044000	3.15856200	-0.35199300
C	-4.00485100	-0.28935700	-0.62017400
H	-3.85644900	-1.07782900	-1.36713900
H	-4.12632100	-0.74324300	0.36650000
H	-4.95399500	0.20119600	-0.87957000

TS_{as}, -749.100111355, ***i*293**

Sc	-0.32766300	0.45242400	-0.14365800
C	0.56339900	2.83225600	0.47432500
H	-0.02406900	3.72666100	0.65565100
H	1.42795300	2.74190300	1.12648500
C	0.72578000	2.46360200	-0.89949300

C	-0.28252500	2.48675500	-1.83637500
H	-1.18164300	3.07692700	-1.69925800
H	-0.10317100	2.11168600	-2.84228200
C	1.13573200	-0.85921300	1.31739100
C	1.99237900	-0.21924200	0.37212100
C	1.66786200	-0.72324900	-0.92253900
C	0.63977600	-1.70559000	-0.77345400
C	0.32769600	-1.80755600	0.61431500
C	3.16718500	0.64851000	0.71477600
H	4.07364900	0.03249800	0.78000100
H	3.05130200	1.13935800	1.68545800
H	3.37289700	1.42247500	-0.03263700
C	2.39200900	-0.43084700	-2.20619200
H	3.09947600	-1.23858700	-2.43551600
H	2.97840800	0.49189300	-2.15514400
H	1.71560200	-0.35260600	-3.06512600
C	0.13641800	-2.58156500	-1.88471800
H	0.89008300	-3.33850200	-2.13905600
H	-0.06694100	-2.02191400	-2.80518000
H	-0.77505600	-3.11827000	-1.61223300
C	-0.50524900	-2.86786300	1.27236100
H	-1.23364600	-3.31535100	0.59278100
H	-1.04498300	-2.50098000	2.15258200
H	0.14451800	-3.68048900	1.62279000
H	1.65960900	1.97871100	-1.17620700
C	1.21981200	-0.72638800	2.81328600
H	0.27155700	-0.96569500	3.30647700
H	1.96837400	-1.41918600	3.21963600
H	1.51454900	0.28012200	3.12748900
C	-1.21313500	1.93225400	1.48397100
C	-2.21870500	1.93428100	0.50099800
H	-0.92142400	0.98561500	1.97425400
H	-1.12550400	2.75332900	2.18525800
C	-2.79903800	0.80543000	-0.14950000
C	-2.60990800	-0.52735000	0.14568400
H	-3.40225600	1.04179700	-1.02692400
H	-2.21146300	-0.79875200	1.12747400
H	-2.55639900	2.90716400	0.15451100
C	-3.33990400	-1.61183700	-0.59571300
H	-2.72115600	-2.49352000	-0.77850300
H	-4.20693400	-1.94854300	-0.01190700
H	-3.70990200	-1.25298300	-1.56151400

TS_{ap}, -749.115522180, ***i*258**

Sc	-0.32964400	0.43281700	-0.10145500
C	-1.47201900	2.78539400	-0.04277400
H	-2.34446500	2.63093400	-0.67837800
H	-1.60225600	3.62034800	0.63893500
C	-0.22657200	2.79846100	-0.76445900
C	0.02482000	2.03685200	-1.87700600
H	-0.79951400	1.54693000	-2.41181600
H	0.96912800	2.09139300	-2.40378800
C	0.97300700	-1.24637200	1.13178500
C	1.71726600	-0.02796600	1.10495000
C	2.10256000	0.22576400	-0.24661600
C	1.54421400	-0.80256400	-1.06438800
C	0.84783100	-1.71198900	-0.21119100

C	2.15025400	0.76883100	2.30385900
H	3.09140700	0.37735000	2.71209600
H	1.41432900	0.73349400	3.11421200
H	2.32607300	1.82180000	2.05974900
C	3.06924800	1.28779600	-0.68017800
H	4.09281500	0.98607800	-0.42227000
H	2.89623500	2.25108100	-0.18699500
H	3.05375500	1.45250900	-1.76098600
C	1.77548900	-1.00382900	-2.53479600
H	2.62008000	-1.68561100	-2.70003900
H	2.01516700	-0.07064000	-3.05255000
H	0.90906600	-1.44971700	-3.03551000
C	0.26379700	-3.02754900	-0.63978800
H	-0.20348300	-2.97709100	-1.62868700
H	-0.48362800	-3.40023900	0.06716700
H	1.05141500	-3.79035600	-0.70006400
H	0.60854700	3.34252400	-0.31977400
C	0.59797600	-2.01251300	2.36498100
H	-0.33667200	-2.57279600	2.25543700
H	1.37849000	-2.74859700	2.59816500
H	0.50568800	-1.36756600	3.24458700
C	-2.11914400	1.53572200	1.53851500
C	-1.80363900	0.15754000	1.64584100
H	-3.11011200	1.80008100	1.17735500
H	-1.76896200	2.16421800	2.35271100
C	-2.29750400	-0.82348800	0.71555300
C	-2.75437900	-0.53273800	-0.54343600
H	-2.15877500	-1.87062600	0.97918800
H	-1.26741100	-0.18666300	2.52366000
C	-3.21076400	-1.54992100	-1.54525200
H	-4.30360800	-1.51747500	-1.64848200
H	-2.80025700	-1.35778400	-2.54415200
H	-2.93339200	-2.56528800	-1.24782900
H	-2.99176700	0.50797600	-0.78498800

TS_{ac}, -944.381951636, ***i*243**

Sc	0.32024400	-0.19461900	-0.19767000
C	-3.46821600	-0.24493000	1.41048900
H	-3.71631600	-1.04193100	0.70109800
H	-3.66203500	-0.64670800	2.41443000
C	-4.32847600	0.95919700	1.16261900
C	-5.22314100	1.06080200	0.17832100
H	-5.39835300	0.24783700	-0.52473100
H	-5.83582300	1.94938300	0.05433300
C	1.51953400	0.94513100	1.62081300
C	1.85799200	1.62175900	0.40956500
C	2.60482600	0.72100900	-0.40688100
C	2.68696900	-0.52797600	0.28045000
C	2.04783600	-0.37912400	1.54609200
C	1.63276500	3.08141800	0.13491300
H	2.40829700	3.68784500	0.62147700
H	0.66825400	3.43692300	0.51312000
H	1.67601500	3.31033900	-0.93410700
C	3.37785700	1.08694800	-1.63862300
H	2.85284700	1.79765100	-2.28541300
H	3.64157300	0.21201400	-2.24102000

H	4.32420800	1.56531100	-1.35377300
C	3.45345800	-1.73933900	-0.17138100
H	4.50834300	-1.66408500	0.12451800
H	3.43858600	-1.86379300	-1.25964600
H	3.06529000	-2.66139300	0.27417100
C	2.10354300	-1.38496200	2.65829800
H	1.84649300	-2.40033900	2.33369900
H	1.44551900	-1.11974100	3.49054900
H	3.12131400	-1.43582400	3.06630900
H	-4.20609300	1.78896000	1.86098100
C	0.90733300	1.59283600	2.82919500
H	0.37574600	0.88002900	3.46811400
H	1.68714500	2.05273400	3.45052500
H	0.20815500	2.39225800	2.56182900
C	-1.95396300	0.08932400	1.34074200
C	-1.04252900	-1.07693200	1.58321300
H	-1.73166700	0.87521500	2.06988400
H	-1.79529800	0.56275200	0.33613700
C	-0.84984400	-2.13200300	0.71512000
C	-1.33081100	-2.23227700	-0.63705400
H	-0.19830800	-2.93851600	1.05762900
H	-0.60129800	-1.15708100	2.57092900
C	-1.49871900	-3.64647700	-1.15938600
H	-2.30837400	-4.14630600	-0.61403900
H	-1.75741200	-3.67123300	-2.22222800
H	-0.58862800	-4.23957600	-1.01440000
H	-2.20035900	-1.60164700	-0.83195500
C	-0.23875500	-1.57467500	-2.36972400
C	0.55686800	-0.40794300	-2.47279400
H	-1.23540600	-1.54143800	-2.80466800
H	0.27787500	-2.51638900	-2.53276100
C	0.00879500	0.91790200	-2.39671000
C	-1.26069400	1.22060800	-1.97428500
H	0.69378200	1.74533400	-2.57216900
H	-1.99919000	0.41819300	-1.91668100
H	1.61313300	-0.51571000	-2.69407500
C	-1.80550500	2.61421600	-1.87881300
H	-2.44871500	2.82390600	-2.74449700
H	-2.42921100	2.75178300	-0.98906000
H	-1.00795600	3.36315000	-1.86850600

′TS$_{ac}$, -944.354955487, ***i*255**

Sc	0.46664700	0.19313000	-0.23865900
C	-4.36013300	0.00747200	1.15293900
H	-4.51965700	-1.07375700	1.05931300
H	-4.11625800	0.20416300	2.20772100
C	-5.60833500	0.74921900	0.77221100
C	-6.70393300	0.18219800	0.26723100
H	-6.77089400	-0.89248000	0.10689600
H	-7.58227900	0.76759800	0.00951800
C	1.60452700	-0.67006800	1.75054900
C	2.26534700	0.54430100	1.38958500
C	2.90584200	0.33599000	0.13110800
C	2.62777000	-1.00291300	-0.28895800
C	1.86758500	-1.63693900	0.73619600
C	2.38370700	1.74122500	2.29201400
H	2.71663100	1.42882000	3.28878300

H	1.44027700	2.28492100	2.42923600
H	3.12365700	2.45340800	1.91972400
C	3.89270300	1.24679500	-0.54074400
H	4.91404000	0.95944200	-0.25852900
H	3.76497600	2.29376800	-0.25719800
H	3.84587900	1.18933400	-1.63423900
C	3.22185000	-1.68165500	-1.49213800
H	4.17473500	-2.16262100	-1.23459100
H	3.43521400	-0.97597400	-2.30188200
H	2.56766500	-2.46120000	-1.89543800
C	1.65273200	-3.11482100	0.87710000
H	1.75519800	-3.64458400	-0.07333100
H	0.68530800	-3.38456300	1.31585700
H	2.41825200	-3.52531800	1.54925200
H	-5.58909300	1.82987600	0.92526700
C	0.93016300	-0.93357300	3.06696500
H	0.13032300	-1.67825000	2.98778800
H	1.65168800	-1.32452200	3.79725100
H	0.50056200	-0.02414200	3.49975900
C	-3.15386500	0.42532400	0.27837500
C	-1.90949900	-0.31096700	0.70732300
H	-3.02699800	1.51272600	0.36740000
H	-3.39822300	0.21996200	-0.76854200
C	-1.30828900	-1.39789700	0.08207100
C	-1.28538300	-1.67070700	-1.31702700
H	-0.68034100	-2.03796200	0.69925500
H	-1.70262100	-0.22991700	1.77914900
C	-0.79915100	-2.98402200	-1.86224900
H	-1.61989600	-3.71463700	-1.85132900
H	-0.47158700	-2.89766900	-2.90437700
H	0.02123800	-3.40393900	-1.27742000
H	-2.13000000	-1.26012200	-1.86623600
C	-0.28849800	0.00600000	-2.49652300
C	-0.96947600	1.15018900	-2.05124600
H	0.81725300	-0.04058700	-2.46972500
H	-0.66393000	-0.56527800	-3.33764600
C	-0.44985600	2.25667900	-1.32171200
C	0.87009000	2.53908000	-1.04414700
H	-1.20311300	2.91537600	-0.88788100
H	1.64608100	2.04676100	-1.63746400
H	-2.04083500	1.16769500	-2.22389600
C	1.27511200	3.80505800	-0.34449300
H	2.13045600	3.67154300	0.32074300
H	1.56131900	4.56534800	-1.08407700
H	0.44931800	4.21524600	0.24612700